Intercomparison Study of

Inductively Coupled Plasma Mass Spectrometry, Thermal Ionization Mass Spectrometry, and Fission Track Analysis

of μBq Quantities of ^{239}Pu in Synthetic Urine

REPORT

for

Department of Energy
Office of International Health Programs (EH-63)

Intercomparison Study of Inductively Coupled Plasma Mass Spectrometry, Thermal Ionization Mass Spectrometry and Fission Track Analysis of μBq Quantities of ^{239}Pu in Synthetic Urine

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August 17, 1997

NIST

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I.

INTRODUCTION, APPROACH and TECHNICAL ISSUES

Introduction

The Department of Energy, Office of International Health Programs (EH-63), is in the process of assisting Marshall Islanders to resettle their islands after five decades. The DOE and the resettled residents require assurances that the radiation dose to residents will not exceed recognized international standards or recommendations. One of the remaining radionuclides that could contribute to internal radiation dose from inhalation and ingestion intake pathways is ^{239}Pu. Since biological samples can be collected to quantitate the body content of radioactive materials or the damage created by exposure to ionizing radiation, the measurement of these parameters by instruments or analytical techniques must be accurately known. The uptake of ^{239}Pu is estimated from the excretion of ^{239}Pu in the urine of an individual. The analytical technique must have sufficient sensitivity to quantify ^{239}Pu at or below a level of 20 μBq/kg.

Until recently, Fission Track Analyses (FTA) of Marshall Islander urine has been the most sensitive measurement technique. Although FTA is very sensitive, it is also expensive and requires long turnaround times. Thermal Ionization Mass Spectrometry (TIMS) has had the potential sensitivity to equal that of FTA and could also provide isotopic information, but has never seriously been used for routine radiobioassay work because of the necessary laborious chemical purifications and rare expertise to knowledgeably operate the instrument. An emerging technology, Inductively Coupled Plasma Mass Spectrometry (ICP-MS), offers great potential as a rapid alternative ultra-sensitive measurement method that is easy to operate and only requires a minimum amount of sample preparation. The attraction of faster, less expensive analyses of very low levels of plutonium in urine at comparable sensitivity motivated the Department of Energy to assess the capabilities of all three of these measurement techniques through this study.

The goal of this phase of the project is to evaluate the state-of-the-art (accuracy and precision) for ^{239}Pu in synthetic urine measurements by inductively coupled plasma (Brookhaven National Laboratory, BNL, and Pacific Northwest National Laboratory, PNNL), thermal ionization mass spectrometry (Los Alamos National Laboratory, LANL) and fission track analysis (BNL) in the concentration range of 18-278 μBq/g for 200g samples of synthetic urine. The major portion of the preparation tasks was performed by the Yankee Atomic Environmental Laboratory (YAEL), in terms of establishing the stability of ^{99m}Tc tracer ^{239}Pu in the synthetic urine, executing the dilutions, confirmational measurements and distributing the samples to participating laboratories. NIST oversaw the development of the work plan, YAEL's preparation of the test materials, and evaluation of the resulting data.

Approach

- o NIST and its subcontractor, YAEL, developed a dilution and measurement confirmation scheme for the production of five replicate ^{239}Pu in synthetic urine

at blank, 18.5, 46.3, 148.4, and 277.7 nBq/g samples for the three participating laboratories.

- NIST, with YAEL, diluted the ^{239}Pu test solutions.

- NIST and YAEL prepared the ^{239}Pu spiked synthetic urine samples, confirmed the dilutions by isotope dilution alpha spectrometry and ^{99m}Tc tracer gamma-spectrometry, and distributed five replicate samples at each concentration blind to Brookhaven, Los Alamos and Pacific Northwest National Laboratories.

- NIST confirmed the YAEL dilution measurements.

- The participating laboratories had two months to report their final measurement data (including negative values) to NIST along with their evaluation of the uncertainties in their measurements.

- NIST evaluated the resulting data to determine the accuracy, precision, sensitivity and limitations of the analyses of ^{239}Pu in synthetic urine:

  - Individual Laboratory Results: (Normality Tests)
    Data Distribution (Test for Measurement control)
    Mean Value (Bias)
    Variance (Precision)
    Identify Potential Measurement Discrepancies

  - Measurement Discrepancies:
    Discuss measurement methodologies with laboratories
    Discuss sources of discrepancies to identify outlying data
    Evaluate likelihood of outlying data

  - Compare Laboratory Performances:
    Data Distribution (Normality Tests)
    Mean Value (Bias)
    Variance (Precision)

  - Resolve Method Dependent Discrepancies:
    Mean Value (Bias)
    Variance (Precision)

  - Technology Evaluation:
    Bias
    Precision
    Minimum Detection Amount.

Technical Issues

A number of technical issues were raised during the design of the intercomparison protocols. These included:

- Stability of the plutonium in glass bottles;
- Stability of the plutonium in the synthetic urine;
- Contamination from plutonium in the reagents used to make the synthetic urine; and
- Adequacy of the synthetic urine as a substitute for natural urine.

Previous experience within the *in vitro* radiobioassay community indicated no particular problems with these issues. However, the issues must be reassessed in this intercomparison because of the extremely low concentrations of plutonium. These issues are addressed using the intercomparison data.

II.

TEST SAMPLE PREPARATION, DILUTION VERIFICATION, TEST SAMPLE UNCERTAINTIES and REPORTING FORMAT

Test Sample Preparation and Distribution Protocols

The following steps describe the methodology used for preparation of ^{239}Pu in synthetic urine performance evaluation (PE) samples.

1. The ^{239}Pu standard was provided by NIST as a Standard Reference Material (SRM 4330A). Five ~ 50 mg aliquots of the SRM underwent alpha spectrometric analysis (sample IDs: 4330A-2 thru 6). The analyses were traced with ^{242}Pu. Counting statistics of ≤2% (1σ cs≤2%) were achieved for each measurement.

2. A 300 g solution of 4N HNO_3 was spiked with ~ 200 µCi of ^{99m}Tc. Sufficient ^{99m}Tc was added to achieve ≤1% counting statistics in a 5 minute counting interval for the dilution described in step 5. Prior to spiking the 4N HNO_3, the ^{99m}Tc concentration in the purchased source was checked via gamma spectrometry of an ~ 1 g aliquot (sample ID: TC-CK1).

3. The ^{239}Pu SRM was diluted by a factor of 707.306 using the nitric acid solution from step 2. The diluted solution was ~ 250 g and was contained in a 500 mL capacity plastic bottle. Sample ID is 4330A-1. The diluted ^{239}Pu concentration was 5.358E-02 Bq/g. Five ~ 10 g aliquots of this dilution were verified via alpha spectrometry traced with ^{242}Pu (1σ cs≤2%). The verification sample IDs are 4330A-1B thru 1F.

4. Five samples, from step 3, were prepared for baseline gamma spectrometric verification by diluting ~ 10 g each of the solution to the required level in the counting container (sample IDs: 4330A-1G thru 1K). The diluent was unspiked 4N HNO_3. The total weight of sample in the counting container will be ~ 70 g with a solution height of 3.8 ± 0.1 cm. All samples prepared for gamma spectrometry were counted in this geometry which is known as the "WATT-1" geometry. A blank 4N HNO_3 sample was also counted.

5. The solution from step 3 was diluted by a factor of 1268.806 using 4N nitric acid. The diluted solution was 3 kg and was contained in a cubitainer. The diluted ^{239}Pu concentration was 4.2231E-05 Bq/g. Sample ID is 4330A-1A.

6. Step 5 dilution was verified via gamma spectrometry (1σ cs≤1%) of five ~70 g aliquots in the WATT-1 geometry (sample IDs: 4330A-1A-1 thru 5). This measurement was compared with the baseline measurement of step 4. One blank aliquot of the 4N HNO_3 diluent also underwent gamma spectrometry. Steps 1 through 6 were performed within a 24 hour period to ensure that significant decay of ^{99m}Tc had not occurred prior to gamma spectrometry. The counting sequence was from the most diluted to the least diluted solution.

7. ^{99m}Tc was added to the solution remaining from step 6 in sufficient quantity (~5 mCi) to achieve ≤1% counting statistics for all subsequent dilutions. The ^{99m}Tc concentration in the purchased source was checked via gamma spectrometry of an ~ 0.1 g aliquot (sample ID: TC-CK2). A baseline gamma spectrometry of the "new" ^{99m}Tc in this solution was performed on five ~ 10 g aliquots diluted with 4N HNO_3 for the WATT-1 geometry (sample IDs: 4330A-1A-6 thru 10). One blank 4N HNO_3 was also counted. This solution is called the stock solution. A new, gravimetric based, ^{239}Pu concentration was recalculated for the stock solution (4.2209E-5 Bq/g). Sample ID of stock solution is 4330A-1A-11.

8. The stock solution from step 7 was diluted by a factor of 911.784 using synthetic urine. This dilution was prepared in a 10 kg cubitainer. The total weight of the diluted solution was 5 kg. The diluted ^{239}Pu concentration was 4.629E-08 Bq/g. Sample ID is PUR-250.

9. Step 8 dilution was verified via gamma spectrometry (1σ cs≤1%) of five aliquots in the WATT-1 geometry (sample IDs: PUR250-A thru E). ^{99m}Tc, added in step 7, was quantified. One blank synthetic urine aliquot was also analyzed.

10. Twenty 200 g aliquots of the solution prepared in step 8 were packaged into 16 oz. glass bottles with an exterior plastic coating. Five bottles each were shipped to two of the three participating labs, whereas ten bottles were shipped to the third lab.

11. The stock solution from step 7 was diluted by a factor of 284.492 using synthetic urine. This dilution was prepared in a 10 kg cubitainer. The total diluted solution weight was 5 kg. The diluted ^{239}Pu concentration was 1.484E-07 Bq/g. Sample ID is PUR-800.

12. Step 11 dilution was verified via gamma spectrometry (1σ cs≤1%) of five aliquots in the WATT-1 geometry (sample IDs: PUR800-A thru E). The analyte quantified was ^{99m}Tc which was added in step 7. One blank synthetic urine aliquot was also analyzed.

13. Twenty 200 g aliquots of the solution prepared in step 11 were packaged into 16 oz. plastic bottles. Five bottles each were shipped to two of the three participating labs, whereas ten bottles were shipped to the third lab.

14. The stock solution from step 7 was diluted by a factor of 151.9716 using synthetic urine. This dilution was prepared in a 10 kg cubitainer. The total diluted solution weight was 5 kg. The diluted Pu-239 concentration was 2.777E-07 Bq/g. Sample ID is PUR-1500.

15. Step 14 dilution was verified via gamma spectrometry (1σ cs≤1%) of five aliquots

in the WATT-1 geometry (sample IDs: PUR1500-A thru E). The analyte quantified was ^{99m}Tc which was added in step 7. One blank synthetic urine aliquot was also analyzed.

16. Twenty 200 g aliquots of the solution prepared in step 14 were packaged into 16 oz. glass bottles. Five bottles each were shipped to two of the three participating labs, whereas ten bottles were shipped to the third lab.

17. The solution from step 14 was diluted by a factor of 15.004 using synthetic urine. This dilution was prepared in a 10 kg cubitainer. The total diluted solution weight was 5 kg. The diluted Pu-239 concentration was 1.851E-08 Bq/g. Sample ID is PUR-100.

18. Step 17 dilution was verified via gamma spectrometry (1σ cs$\leq$1%) of five aliquots in the WATT-1 geometry (sample IDs: PUR100-A thru E). The analyte quantified was ^{99m}Tc which was added in step 7. One blank aliquot was also analyzed. Steps 7 through 18 were performed within a 24 hour period to ensure that significant decay of ^{99m}Tc had not occurred prior to gamma spectrometry. The counting sequence was from the most diluted to the least diluted PE sample.

19. Twenty 200 g aliquots of the solution prepared in step 17 were packaged into 16 oz. glass bottles. Five bottles each were shipped to two of the three participating labs, whereas ten bottles were shipped to third lab.

20. Twenty 200 g aliquots of the blank synthetic urine were also packaged into 16 oz. glass bottles. Five bottles each were shipped to two of the three participating labs, whereas ten bottles were shipped to the third lab.

21. The 200 g shipping aliquots of all the concentration levels were prepared 12 to 24 hours after the preparation of the PE materials.

ATTACHMENT I

REQUIREMENTS FOR CONFORMANCE

1. Two weights were recorded for each weighing. The precision of the two weights were within 0.5 percent. The mean of the two weights were used to calculate the gravimetric concentrations.

2. Counting statistics of 1% or better was achieved for all gamma spectrometric measurements. Counting statistics of 2% or better was achieved for all alpha spectrometric measurements.

3. All bottles packaged for shipping, including blanks, were assigned random ID numbers from 1 to 100. Higher concentration solutions, which were sent for fission track analysis, were labeled "high concentration."

4. 30 kg of synthetic urine was prepared in batches of 2 kg each. The batches were combined in a carboy and equilibrated for 24 hours. The synthetic urine was filtered through a 0.45μ filter (Gelman HT 450).

5. All glass bottles, used for shipping, were soaked for 72 h each in 0.1M disodium EDTA, 2M HNO_3 and 2M HCl. The bottles were rinsed with high purity deionized water and air dried.

6. All prepared solutions were shaken for at least 15 minutes before removing any aliquots.

7. All spikes, except the spike in step 16 were dispensed into the diluents via pycnometers. A 500-g poly bottle was used to deliver the 333.3 g spike in step 16.

8. The Mettler AE 163 analytical balance was used to determine the weights of the added spikes with the exception of the spike in step 16. The Mettler PM16-N balance was used to determine the weight of the spike dispensed in step 16. For the dilutions described in steps 10 and 13, multiple dispensations of the spikes were required due to the overall weight limit of 26 g on the AE 163 balance.

9. NIST prepared the certificates of content for the PE samples. The attached flowchart illustrates of the protocol described above.

ATTACHMENT II

EQUIPMENT AND SUPPLIES

1. GM survey meter
2. Log book, calculator, ruler, markers & pens
3. Gloves (L, M & S), safety glasses and lab coats
4. Absorbent paper, paper towels and kimwipes
5. Radwaste bin
6. Non contaminated waste bin
7. Decon spray cans (hand and surface)
8. File for scoring ampoule
9. Plastic protectors for ampoule tip
10. Fifty pycnometers with elongated tips.
11. 500 mL and 1 gal. plastic bottles
12. Four 10L (2.5 gal) cubitainers and boxes
13. 50 kg carboy
14. 50 4 oz. plastic jars (counting containers for ^{99m}Tc) and plastic bags
15. Labels (w/ radioactive symbol) for ^{99m}Tc counting containers
16. Fifty gamma spec. measurement request forms (YELF 1101.1)
17. Duct, packing & electrical tapes
18. 25 HazMat multi pack shippers containing a 100 16 oz. glass bottles with exterior plastic coating.
19. 100 labels for shipping bottles
20. 25 FedEx Dangerous Goods Airbills, address labels and "Corrosive" labels
21. Reverse electrode germanium detector (40% relative efficiency)
22. Octet PC Alpha Spectrometer
23. Mettler AE 163 analytical balance with 5 digit precision and GA42 printer.
24. Mettler PM16-N top loader balance with 1 digit precision.

REAGENTS

1. High purity deionized water
2. 4M nitric acid - 4 kg
3. 0.1M Disodium EDTA
4. 2M nitric acid
5. 2M hydrochloric acid
6. Synthetic Urine - 30 kg (see attached recipe)
7. Pu-239 SRM
8. Tc-99m
9. Standardized Pu-242

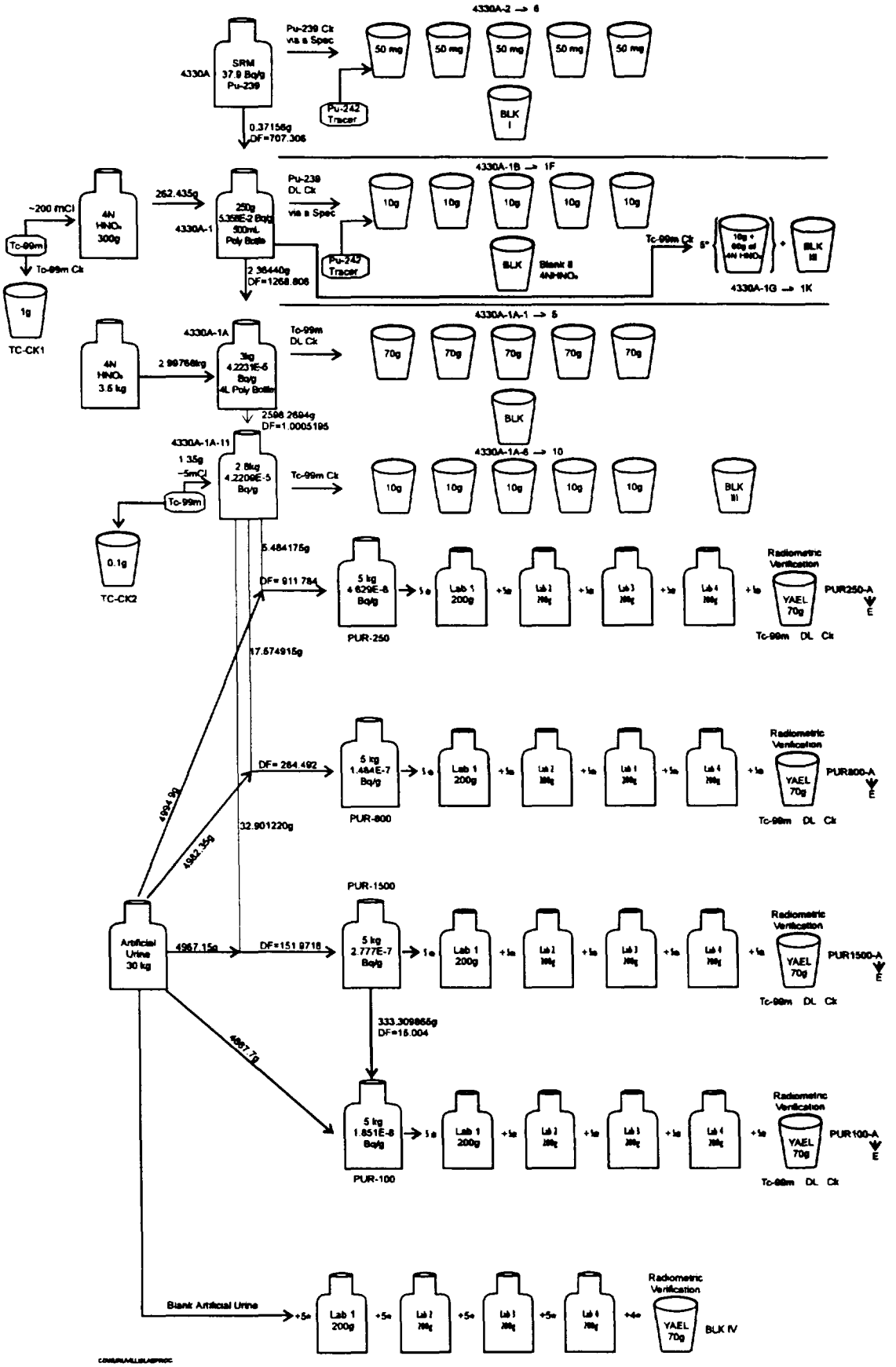
RECIPE FOR SYNTHETIC URINE

Component	g/kg
Urea	16.00
NaCl	2.32
KCl	3.43
Creatinine	1.10
Na_2SO_4 (anhydrous)	4.31
Hippuric Acid	0.63
NH_4Cl	1.06
Citric Acid	0.54
$MgSO_4$ (anhydrous)	0.46
$NaH_2PO_4 \bullet H_2O$	2.73
$CaCl_2 \bullet 2H_2O$	0.63
Oxalic Acid	0.02
Lactic Acid	0.094
Glucose	0.48
$Na_2SiO_3 \bullet 9H_2O$	0.071
Pepsin	0.029
Conc. Nitric Acid	50.00
Yellow Food Color (optional)	0.06

Fn:kinn/yael/puurine.pap/September 11, 1997

Attachment III

SAMPLE PREPARATION DESIGN


4330A-2 → 6
SRM
37.9 Bq/g
Pu-239
4330A
Pu-239 Clx
via a Spec
50 mg
50 mg
50 mg
50 mg
50 mg
BLK
I
Pu-242
Tracer
0.37156g
DF=707.306
4330A-1B → 1F
4330A-1
250g
5.35E-2 Bq/g
500mL
Poly Bottle
262.435g
2.36440g
DF=1268.808
Pu-239
DL Clx
via a Spec
10g
10g
10g
10g
10g
BLK
Blank II
4N-HNO3
Pu-242
Tracer
Tc-99m Clx
4330A-1G → 1K
BLK
III
~200 mCi
Tc-99m
4N
HNO3
300g
Tc-99m Clx
1g
TC-CK1
4330A-1A-1 → 5
4330A-1A
3kg
4.2231E-6
Bq/g
4L Poly Bottle
4N
HNO3
3.6 kg
2.99764kg
Tc-99m
DL Clx
70g
70g
70g
70g
70g
BLK
2598.2694g
DF=1.0005195
4330A-1A-6 → 10
4330A-1A-11
2 Bkg
4.2209E-5
Bq/g
1.35g
~5mCi
Tc-99m
Tc-99m Clx
10g
10g
10g
10g
10g
BLK
III
0.1g
TC-CK2
5.484175g
DF= 911.784
5 kg
4.629E-6
Bq/g
PUR-250
Lab 1
200g
Lab 2
200g
Lab 3
200g
Lab 4
200g
Radiometric
Verification
YAEL
70g
PUR250-A
Tc-99m DL Clx
17.574915g
DF= 284.492
5 kg
1.484E-7
Bq/g
PUR-800
PUR800-A
4994.9g
4982.35g
32.901220g
PUR-1500
Artificial
Urine
30 kg
4967.15g
DF=151.9718
5 kg
2.777E-7
Bq/g
PUR1500-A
333.309865g
DF=15.004
4967.7g
5 kg
1.851E-8
Bq/g
PUR-100
PUR100-A
Blank Artificial Urine
BLK IV

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Attachment IV

SRM 4330A Certificate

National Institute of Standards & Technology

Certificate

Standard Reference Material 4330A
Plutonium-239 Radioactivity Standard

This Standard Reference Material (SRM) consists of radioactive plutonium-239 nitrate and nitric acid dissolved in 5 mL of distilled water. The solution is contained in a flame-sealed NIST borosilicate-glass ampoule. The SRM is intended for the calibration of alpha-particle counting instruments and for the monitoring of radiochemical procedures.

Radiological Hazard

The SRM ampoule contains plutonium-239 with a total activity of approximately 210 Bq. Plutonium-239 decays by alpha-particle emission. None of the alpha particles escape from the SRM ampoule. During the decay process X-rays and gamma rays with energies from 10 keV to 1 MeV are also emitted. Most of these photons escape from the SRM ampoule but their intensities are so small that they do not represent a radiation hazard. Approximate unshielded dose rates at several distances (as of the reference time) are given in note [a]*. The SRM should be used only by persons qualified to handle radioactive material.

Chemical Hazard

The SRM ampoule contains nitric acid (HNO_3) with a concentration of 3 moles per liter of water. The solution is corrosive and represents a health hazard if it comes in contact with eyes or skin. If the ampoule is to be opened to transfer the solution, the recommended procedure is given on page 2. The ampoule should be opened only by persons qualified to handle both radioactive material and strong acid solution.

Storage and Handling

The SRM should be stored and used at a temperature between 5 and 65 °C. The solution in an unopened ampoule should remain stable and homogeneous until at least December 2005.

The ampoule (or any subsequent container) should always be clearly marked as containing radioactive material. If the ampoule is transported it should be packed, marked, labeled, and shipped in accordance with the applicable national, international, and carrier regulations. The solution in the ampoule is a dangerous good (hazardous material) both because of the radioactivity and because of the strong acid.

Preparation

This Standard Reference Material was prepared in the Physics Laboratory, Ionizing Radiation Division, Radioactivity Group, J.M.R. Hutchinson, Group Leader. The overall technical direction and physical measurements leading to certification were provided by L.L. Lucas of the Radioactivity Group.

The support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the Standard Reference Materials Program by N.M. Trahey.

Gaithersburg, Maryland 20899
January 1996

Thomas E. Gills, Chief
Standard Reference Materials Program

*Notes and references are on pages 5 and 6.

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Recommended Procedure for Opening the SRM Ampoule

1) If the SRM solution is to be diluted, it is recommended that the diluting solution have a composition comparable to that of the SRM solution.

2) Wear eye protection, gloves, and protective clothing and work over a tray with absorbent paper in it. Work in a fume hood. In addition to the radioactive material, the solution contains strong acid and is corrosive.

3) Shake the ampoule to wet all of the inside surface of the ampoule. Return the ampoule to the upright position.

4) Check that all of the liquid has drained out of the neck of the ampoule. If necessary, gently tap the neck to speed the process.

5) Holding the ampoule upright, score the narrowest part of the neck with a scribe or diamond pencil.

6) Lightly wet the scored line. This reduces the crack propagation velocity and makes for a cleaner break.

7) Hold the ampoule upright with a paper towel, a wiper, or a support jig. Position the scored line away from you. Using a paper towel or wiper to avoid contamination, snap off the top of the ampoule by pressing the narrowest part of the neck away from you while pulling the tip of the ampoule towards you.

8) Transfer the solution from the ampoule using a pycnometer or a pipet with dispenser handle. NEVER PIPETTE BY MOUTH.

9) Seal any unused SRM solution in a flame-sealed glass ampoule, if possible, to minimize the evaporation loss.

See also reference [4]*.

*Notes and references are on pages 5 and 6.

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PROPERTIES OF SRM 4330A

(Certified values are shown in bold type)

Source identification number	NIST SRM 4330A		
Physical Properties:			
Source description	Liquid in flame-sealed NIST borosilicate-glass ampoule		
Ampoule specifications	Body outside diameter Wall Thickness Barium content Lead-oxide content Other heavy elements	(16.5 ± 0.5) mm (0.60 ± 0.04) mm Less than 2.5% Less than 0.02% Trace quantities	
Solution density	**(1.0895 ± 0.002) g·mL^{-1} at 24.9 °C** [b]*		
Solution mass	Approximately 5.5 g		
Chemical Properties:			
Solution composition	Chemical Formula	Concentration (mol·L^{-1})	Mass Fraction (g·g^{-1})
	H_2O HNO_3 HCl $^{239}Pu^{+6}$	51 2.8 0.02 8×10^{-8}	0.84 0.16 0.0007 2×10^{-8}
Radiological Properties:			
Radionuclide	**Plutonium-239**		
Reference time	**1200 EST, 4 December 1995**		
Massic activity of the solution [c]	**37.90 Bq·g^{-1}**		
Relative expanded uncertainty (k=2)	**0.72%** [d] [e]		
Alpha-particle-emitting impurities	None detected [f]		
Photon-emitting impurities	None detected [g]		
Half lives used in the decay corrections	Plutonium-239: (24119 ± 26) a [h]		
Calibration method	NIST "0.1π"α defined-solid-angle counter with scintillation detector and two 4πα liquid-scintillation counting systems		

*Notes and references are on pages 5 and 6.

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EVALUATION OF THE UNCERTAINTY OF THE MASSIC ACTIVITY [d]*

Input Quantity x_i, the source of uncertainty (and individual uncertainty components where appropriate)	Method Used To Evaluate $u(x_i)$, the standard uncertainty of x_i (A) denotes evaluation by statistical methods (B) denotes evaluation by other methods	Relative Uncertainty Of Input Quantity, $u(x_i)/x_i$, (%) [i]	Relative Sensitivity Factor, $\lvert\partial y/\partial x_i\rvert \cdot (x_i/y)$ [j]	Relative Uncertainty Of Output Quantity, $u_i(y)/y$, (%) [k]
Massic alpha-particle emission rate, corrected for background and decay	Standard deviation of the mean for 10 sets of "0.1π"α measurements and 15 sets of 4πα liquid-scintillation measurements (A)	0.05	1.0	0.05
Decay correction for plutonium-239	Standard uncertainty of the half life (A)	0.11 [m]	0.0005 [n]	0.00005
Decay-scheme data	Standard uncertainty of the probability of decay by alpha-particle emission (A)	0.001	1.0	0.001
Extrapolation of alpha-particle-count-rate-versus-energy to zero energy	Estimated (B)	0.25	1.0	0.25
Gravimetric measurements	Estimated (B)	0.10	1.0	0.10
Live-time [p]	Estimated (B)	0.10	1.0	0.10
Alpha-particle detection efficiency of scintillators	Estimated (B)	0.10	1.0	0.10
Geometry of "0.1π"α counter	Estimated (B)	0.25	0.4	0.10
Alpha-particle-emitting impurities	Limit of detection (B) [q]	100.	0.001	0.10
Photon-emitting impurities	Limit of detection (B) [q]	100.	0.001	0.10
Relative Combined Standard Uncertainty of the Output Quantity, $u_c(y)/y$, (%)				0.36
Coverage Factor, k				x 2
Relative Expanded Uncertainty of the Output Quantity, U/y, (%)				0.72

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*Notes and references are on pages 5 and 6.

NOTES

[a] The Sievert is the SI unit for dose equivalent. See reference [1]. One μSv is equal to 0.1 mrem.

Distance from Ampoule (cm):	1	30	100
Approximate Dose Rate (μSv/h):	<0.1	-	-

[b] The stated uncertainty is two times the standard uncertainty.

[c] **Massic activity** is the preferred name for the quantity activity per unit mass. See reference [1].

[d] The reported value, y, of massic activity (activity per unit mass) at the reference time was not measured directly but was derived from measurements and calculations of other quantities. This can be expressed as $y = f(x_1, x_2, x_3, \ldots x_n)$, where f is a mathematical function derived from the assumed model of the measurement process.

The value, x_i, used for each input quantity i has a **standard uncertainty**, $u(x_i)$, that generates a corresponding uncertainty in y, $u_i(y) \equiv |\partial y/\partial x_i| \cdot u(x_i)$, called a **component of combined standard uncertainty** of y.

The **combined standard uncertainty** of y, $u_c(y)$, is the positive square root of the sum of the squares of the components of combined standard uncertainty.

The combined standard uncertainty is multiplied by a **coverage factor** of $k = 2$ to obtain U, the **expanded uncertainty** of y.

Since it can be assumed that the possible estimated values of the massic activity are approximately normally distributed with approximate standard deviation $u_c(y)$, the unknown value of the massic activity is believed to lie in the interval $y \pm U$ with a level of confidence of approximately 95 percent.

For further information on the expression of uncertainties, see references [2] and [3].

[e] The value of each standard uncertainty component, and hence the value of the expanded uncertainty itself, is a best estimate based upon all available information, but is only approximately known. That is to say, the "uncertainty of the uncertainty" is large and not well known. This is true for uncertainties evaluated by statistical methods (e.g., the relative standard deviation of the standard deviation of the mean for the massic count rate is approximately 50%) and for uncertainties evaluated by other methods (which could easily be over estimated or under estimated by substantial amounts). The unknown value of the expanded uncertainty is believed to lie in the interval $U/2$ to $2U$ (i.e., within a factor of 2 of the estimated value).

[f] Estimated limits of detection for alpha-particle-emitting impurities are:
0.04 $\alpha \cdot s^{-1} \cdot g^{-1}$ for energies less than 4.9 MeV and
0.001 $\alpha \cdot s^{-1} \cdot g^{-1}$ for energies greater than 5.2 MeV.

From mass-spectrometric measurements performed by the supplier, the massic activities of other detected radionuclides (in $Bq \cdot g^{-1}$ at the reference time) are:
^{240}Pu: 0.002; ^{241}Pu: ≈0.02; ^{242}Pu: ≈0.000003; ^{241}Am: ≈0.0009
From the photon measurements below, we have ^{241}Am: ≤0.0006

[g] Estimated limits of detection for photon-emitting impurities are:
0.000200 $\gamma \cdot s^{-1} \cdot g^{-1}$ for energies between 42.5 and 90 keV,
0.000080 $\gamma \cdot s^{-1} \cdot g^{-1}$ for energies between 102 and 125 keV,
0.000030 $\gamma \cdot s^{-1} \cdot g^{-1}$ for energies between 133 and 1456 keV, and
0.000008 $\gamma \cdot s^{-1} \cdot g^{-1}$ for energies between 1465 and 3500 keV,
provided that the photons are separated in energy by 4 keV or more from photons emitted in the decay of plutonium-239.

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[h] The stated uncertainty is the standard uncertainty. See reference [5].

[i] Relative standard uncertainty of the input quantity x_i.

[j] The relative change in the output quantity y divided by the relative change in the input quantity x_i. If $|\partial y/\partial x_i| \cdot (x_i/y) = 1.0$, then a 1% change in x_i results in a 1% change in y. If $|\partial y/\partial x_i| \cdot (x_i/y) = 0.05$, then a 1% change in x_i results in a 0.05% change in y.

[k] Relative component of combined standard uncertainty of output quantity y, rounded to two significant figures or less. The relative component of combined standard uncertainty of y is given by $u_i(y)/y \equiv |\partial y/\partial x_i| \cdot u(x_i)/y = |\partial y/\partial x_i| \cdot (x_i/y) \cdot u(x_i)/x_i$. The numerical values of $u(x_i)/x_i$, $|\partial y/\partial x_i| \cdot (x_i/y)$, and $u_i(y)/y$, all dimensionless quantities, are listed in columns 3, 4, and 5, respectively. Thus, the value in column 5 is equal to the value in column 4 multiplied by the value in column 3. The input quantities are independent, or very nearly so. Hence the covariances are zero or negligible.

[m] The relative standard uncertainty of $\lambda \cdot t$ is determined by the relative standard uncertainty of λ (i.e., of the half life). The relative standard uncertainty of t is negligible.

[n] $|\partial y/\partial x_i| \cdot (x_i/y) = |\lambda \cdot t|$

[p] The live time is determined by counting the pulses from a gated oscillator.

[q] The standard uncertainty for each undetected impurity that might reasonably be expected to be present is estimated to be equal to the estimated limit of detection for that impurity, i.e. $u(x_i)/x_i = 100\%$. $|\partial y/\partial x_i| \cdot (x_i/y) = \{$(response per Bq of impurity)/(response per Bq of Pu-239)$\} \cdot \{$(Bq of impurity)/(Bq of Pu-239)$\}$. Thus $u_i(y)/y$ is the relative change in y if the impurity were present with a massic activity equal to the estimated limit of detection.

REFERENCES

[1] International Organization for Standardization (ISO), *ISO Standards Handbook - Quantities and Units*, 1993. Available from the American National Standards Institute, 11 West 42nd Street, New York, NY 10036, U.S.A. 1-212-642-4900.

[2] International Organization for Standardization (ISO), *Guide to the Expression of Uncertainty in Measurement*, 1993. Available from the American National Standards Institute, 11 West 42nd Street, New York, NY 10036, U.S.A. 1-212-642-4900. (Listed under ISO miscellaneous publications as "ISO Guide to the Expression 1993".)

[3] B. N. Taylor and C. E. Kuyatt, *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*, NIST Technical Note 1297, 1993. Available from the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20407, U.S.A.

[4] National Council on Radiation Protection and Measurements Report No. 58, *A Handbook of Radioactivity Measurements Procedures*, Second Edition, 1985. Available from the National Council on Radiation Protection and Measurements, 7910 Woodmont Avenue, Bethesda, MD 20814 U.S.A.

[5] Evaluated Nuclear Structure Data File (ENSDF), December 1995.

Dilution Verification

Although dilutions of the sequential solutions could be calculated from the gravimetric determinations, it is good laboratory practice to verify the dilutions with measurements. It is particularly imperative to confirm the dilutions for this exercise because these are the first certified test materials of plutonium in the nBq/g range. Known quantities of ^{99m}Tc were added to the plutonium reference materials, and the subsequent dilutions were confirmed by measuring the reference and diluted materials with a HPGe detector. Table 1 summarizes the results of the verification measurements for the dilutions listed in the first column. The second and third columns indicates the percent difference between measured and gravimetrically determined dilution factors and the associated 1 sigma total propagated uncertainties. The fourth column indicates the acceptance limit for the t test determination of any statistically significant difference between the measured and gravimetric dilution factors. As a whole, the measured dilution factors are not statistically different from the gravimetric dilution factors at the $\alpha = 0.5$ level.

Table 1

Dilution	Number of Replicate Sources	Percent Difference between Measured and Gravimetric Dilution Factors	Total Propagated 1 Sigma (%)	$t_{0.975}$ Test (%)
SRM 4330A to 4330A-1	5	-3.11	2.62	± 3.26
4330A-1 to 4330A-1A	5	-2.58	3.21	± 3.98
4330A-1A-11 to PUR1500	5	-2.81	2.57	± 3.19
PUR1500 TO PUR100	5	-1.87	2.58	± 3.21
4330A-1A-11 to PUR250	5	-3.76	2.60	± 3.23
4330A-1A-11 to PUR800	5	-3.03	2.50	± 3.11

Test Sample Uncertainties

Table 2 summarizes the test sample uncertainties. As a result of acceptable measurement verification of the gravimetric dilution factors, the only additional uncertainty component that was propagated with the total relative uncertainty of the reference materials is from the gravimetric dilutions. These uncertainties were propagated as the root-sum-of-squares (Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results, B.N. Taylor and C.E. Kuyatt, NIST Technical Note 1297, NIST, Gaithersburg, MD, 1994) and reported as the relative expanded uncertainty for K = 2.

Table 2

	Uncertainty Components			
Sample	Reference Material Total Uncertainty	Gravimetric	Sample Total Relative Uncertainty	Relative Expanded Uncertainty
Identification Number	1 s_m, percent	1 s, percent	1 s_m, percent	$2s_m$, percent
SRM 4330A	0.36	-	0.36	0.7
4330A-1	0.36	0.14	0.4	0.8
4330A-1A	0.39	0.14	0.4	0.8
4330A-1A-11	0.41	0.14	0.4	0.9
PUR1500	0.44	0.14	0.5	1.0
PUR100	0.46	0.14	0.5	1.0
PUR250	0.44	0.14	0.5	1.0
PUR800	0.44	0.14	0.5	1.0

Reporting Format

The following reporting format was provided to the participating laboratories to organize the relevant information on their measurement protocols, results and the associated uncertainties.

Results of Measurement
^{239}Pu in Synthetic Urine

1. Please use this data reporting form for the submission of analytical results. Twenty-five samples of ^{239}Pu spiked unstable synthetic urine (< 74000 nBq/sample) have been provided for this study. Because the long-term stability of the plutonium in the synthetic urine has not been determined, please analyze the total content of each bottle of sample (i.e., use the total content of a bottle for a single measurement), and report both the total activity and massic activity for each measurement result. Since the long-term stability of the samples has not been determined, it is strongly advised that each sample bottle is rinsed with > 3 M nitric acid, and the rinse solution be analyzed with the sample. The reference date and time for your reported results is:

12:00 noon EST, February 26, 1997

2. Report ^{239}Pu measurements in $Bq \cdot g^{-1}$ of solution. Report total combined standard uncertainty as 1s (%).

Sample Number	Total Activity (Bq) in each Bottle	Massic Activity ($Bq \cdot g^{-1}$)	Uncertainty (% 1s)

3. State the ±1s "standard uncertainty" components (random and systematic) which comprise the combined standard uncertainty. These may include, but are not limited to the following:

   Uncertainty due to calibration factor/efficiency =_____%.
   Uncertainty due to dilutions/source preparation =_____%.
   Uncertainty due to impurity corrections =_____%.
   Uncertainty due to tracer calibration =_____%.
   Uncertainty due to gravimetric measurements =_____%.
   Uncertainty due to spectral interferences =_____%.
   Others; please describe.

   _____
   _____
   _____

4. Describe in detail how the TEST samples were used, (i.e., give a detailed chronological description of the handling of the samples from the time they were opened to the time of reporting of results). This should include a description of solution transfer methodologies, chemical yield tracer additions, chemical separation used, measurement source preparation, storage of samples, etc. **Please attach a separate page if necessary**.

5. Describe the type of measurement system used, including a general description of its operation. Also indicate the type of analysis software utilized for any calculations and/or corrections applied to raw measurement data if applicable.

6. Using actual measurement data, calibration factors, corrections, etc., give a sample calculation showing how the massic activity and uncertainty values reported in section 2 were determined. Identify all values used, e.g., efficiency, calibration factors, mass, volume, decay correction, etc. **Attach a separate sheet if necessary**.

7. Please provide any additional information about your measurements that needs to be considered for the interpretations of the results.

8. The deadline for submitted results is May 16, 1997. Please address results and technical questions to:

Kenneth G.W. Inn
NIST
245/C114
Gaithersburg, MD 20899

Phone: 301-975-5541
Fax: 301-869-7682
email: kenneth.inn@nist.gov

III.

NATIONAL LABORATORIES' ANALYTICAL METHODS

Attachments V, VI, VII and VIII are the reports of the analytical methods used by the national laboratories, the measurement results and the associated uncertainties. Table 3 summarizes the major analytical steps used by each laboratory.

Table 3

	BNL ICP-MS	BNL FTA	LANL	PNNL
Sample Preparation	Calcium Rhodizonate (pH > 9.5), coppt with EtOH, H_2O_2/HNO_3 microwave digestion, heat to dryness	Calcium Rhodizonate (pH > 9.5), coppt with EtOH, H_2O_2/HNO_3 microwave digestion, heat to dryness	Calcium Phosphate coppt from H_2O_2 solution, dissolve in 8 N HNO_3	Calcium Phosphate coppt, HNO_3/H_2O_2 dissolution
Yield Monitor	^{242}Pu	Batch Yield Determination	^{242}Pu	^{244}Pu
Chemical Separations	Fe^{++} + NO_3-, AG1X4, 8N HNO_3 & HCl wash, HI/HCl elution, heat to dry, 8 N HNO_3	Fe^{++} + NO_3-, AG1X4, 8N HNO_3 & HCl wash, HI/HCl elution, heat to dry, 8 N HNO_3, micro anion exchange	AG1X4, 8 N HNO_3 wash, 0.36 N HCl - 0.01 M HF elute, electrodeposit from $NaHSO_4$ soln, strip w/HF & HNO_3, AG MP-1, 8 N HNO_3, AG MP-1, 8 N HNO_3 wash, 0.5 N HCl & HI :HCl (1:9 vol.), AG-MP-1, H_2O_2-HCl wash, HBr elution	2 N HNO_3 TEVA-Spec micro column, 6 N HCl wash, DI elution

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Source Preparation	100 µL 4 N HNO_3, filtered through 2 µm polypropylene filter	3 drops dried on Suprasil slides	Pu electrodeposited w/DNS from NH_4Cl soln, over deposited w/DNS	H_2O vol. reduction to 0.5 mL
Instrumental Method	HP 4500, µ-concentric nebulizer, torchshield, tuned for Tl; 108.5 sec analysis	9 X 1016 n/cm^2 FTA, HF etch, microscope counting	Single stage TIMS, 6 min analysis	VG Plasma Quad II+ with "S-option" membrane desolvation, µ-concentric Cetac nebulizer MCN-6000; 20 µL/min, 10 min analysis

DNS = dihydrogen dinitro sulfato platinate (II)

Attachment V

BNL ICP-MS Report

2007
5810
Department of Advanced Technology
Building 703M
E-MAIL KAPLAN@BNL.GOV

June 6, 1997

Dr. Kenneth G.W. Inn
NIST
245/C114
Gaithersburg, MD 20899

Dear Ken:

Many thanks for calling us concerning the fission track analytical and ICPMS data we reported to you on May 22nd. In this regard, please note the following corrections which we discussed this morning concerning data from fission track analyses:

1. For sample PUR0297-53, please change the reported massic activity from 31.3 μBq/kgm to 31.1 μBq/kgm,

2. With reference to the first paragraph on page 2 of my letter, we incorrectly identified the two samples lost during processing. Instead of using your sample identification numbers, we reported our internal fission track numbers. Thus what we reported earlier as sample PUR0297-34 was in reality your sample PUR0297-33. In addition, reported sample PUR0297-21 was actually PUR0297-62.

Samples PUR0297-12,93 were found to have many fewer tracks than expected (i.e., since they were part of the 5 replicates labeled as containing more than 1 fCi). As we discussed during earlier phone conversations, our FTA calibration curve has a maximum of about 500 aCi since in the normal course of our studies we usually do not encounter samples with much greater activity. For each these samples we placed droplets from our small column in pairs at three locations on the quartz substrate (instead of placing all six drops at a single location). Despite this precaution we still found more than 500 tracks for the first pairs, many of which were overlapping. Hence our initial estimates are known to be lower than expected. These samples have been recounted and show no significant changes in track count. Overlapping is attributable to the manner in which samples evaporate on the substrate, and increases with the amount of ^{240}Pu in the sample. Our best conclusion is that counts of samples PUR0297-12,93 were lower than

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expected, and we attribute this to our inability to distinguish individual tracks when they overlap in large numbers.

As mentioned, samples PUR0297-41,50 were on the same quartz substrate which was discolored (brown) when returned from the reactor. All other slides in the batch appeared normal except one, which contained two blanks and a flux monitor, and was returned discolored and deformed. We were unable to determine whether the discoloration could be related to objects on the slide (some recorded as tracks), and decided to report our findings as acceptable. These samples will also be recounted.

We are perplexed by sample PUR0297-41 for another reason. As we mentioned in our conversation, the location of this sample on the quartz substrate may have originally been incorrectly indicated in our logs. We surmise that we correctly identified the sample by comparing the pattern of tracks actually found with a sketch of the evaporated sample in our data book. Under normal operating procedures we would have reanalyzed this sample before reporting a result.

Records for samples PUR0297-51,91 have been reviewed and all appears in order. Under our normal protocol to minimize chances of false positives, we would have reanalyzed sample PUR0297-51 before reporting a result.

Apropos the ICPMS data, Rich Pietrzak is sending you a revised letter today. To summarize his findings, sample PUR0297-46 had a uniquely low chemical yield when compared to the entire set. The consequence of this is that the MDL for this sample alone is estimated at 5 μBq. Records for sample PUR0297-36 have been reviewed and all appears in order. There were also two typographical errors in our original letter. On page 2, item 3.5, change 12% to 9%. On page 3, next to last line from bottom, should read 55.6 μBq.

Thanks again for your interest. We look forward to hearing from you concerning these results.

Very truly yours,

Anant Moorthy, Ph.D.

Richard Pietrzak

Edward Kaplan, Ph.D., Group Leader
Radiological Sciences Division

EK/mcb

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Department of Advanced Technology
Building 703M

June 6, 1997

Dr. Kenneth G.W. Inn
NIST
245/C114
Gaithersburg, MD 20899

Dear Ken:

We are taking the liberty of reporting the results of the samples you recently sent in letter format, rather than using the forms. Please note that the following correspond only to the samples analyzed via the mass spectroscopy analytical process.

Sample ID	Pu-239 µBq	Uncertainty µBq Lower (at 1 sigma)	Uncertainty µBq Upper (at 1 sigma)	Pu-239 µBq/kg
PUR0297-16	3.4	3.1	3.6	16
PUR0297-18	0.1	-0.2	0.3	0.3
PUR0297-26	9.0	8.7	9.2	40
PUR0297-29	7.7	7.5	7.9	38
PUR0297-32	8.5	8.2	8.7	39
PUR0297-35	54.9	54.6	55.1	257
PUR0297-36	9.6	9.4	9.9	43
PUR0297-44	28.4	28.1	28.6	136
PUR0297-46*	-3.8	-4.1	-3.6	-19
PUR0297-52	31.3	31.1	31.6	149
PUR0297-54	8.8	8.6	9.1	41.5
PUR0297-57	55.6	55.3	55.8	263
PUR0297-58	3.3	3.1	3.6	15
PUR0297-65	2.8	2.6	3.0	12
PUR0297-70	58.1	57.9	58.4	255
PUR0297-71	-0.8	-1.1	-0.6	-4.1
PUR0297-74	28.3	28.1	28.6	134
PUR0297-75	3.6	3.3	3.8	16
PUR0297-79	55.9	55.7	56.1	257
PUR0297-81	29.2	29.0	29.4	136
PUR0297-84	57.9	57.7	58.1	262
PUR0297-85	9.4	9.1	9.6	44
PUR0297-87	29.7	29.5	30.0	138
PUR0297-92	0.6	0.3	0.8	3
PUR0297-100	0.2	-0.1	0.4	0.7

*Low chemical yield gives an estimated MDL of 5 µBq.

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Our detection limit is approximately 50 aCi or 2 μ Bq. Values below this limit as well as negative results are included in the table for the benefit of statistical evaluation.

The following correspond to the items on your reporting forms.

Item #3:

1) Pu standard certification uncertainty: Pu-239 5%
   Pu-242 0.74%

2) Pu standard preparation error: 3%
   (includes dilution error)

4) Mass Spectroscopy counting error: 3%

5) Pu recovery error in the chemistry procedure: 9%

   Two major areas:
   1) Co-precipitation step: 5%
   2) Anion exchange column separation: 7%

Item #4: Procedure

The tapes around the glass NIST sample bottle caps were removed and the individual weights were noted. The samples were transferred to plastic containers for the co-precipitation step. To each empty bottle, 5 ml of conc. HNO_3 was added and the acid was sloshed around. They were stored for later addition to the samples. Synthetic urine blanks (a total of seven blanks) and spikes (a total of 16 spikes from 100 aCi to 2000 aCi) of volume equal to those of NIST samples were also analyzed along with the samples. Nominally equal amounts by weight of a Pu-242 tracer solution were added to both samples and synthetic urine blanks and spikes, and were stirred and allowed to equilibrate.

The pH of each sample was verified to be less than 2 and rhodizonic acid was added to each sample (100 mg for each 100 ml of sample) and stirred for 15 minutes. Then pH was adjusted to greater than 9.5 to precipitate calcium rhodizonate that carries the plutonium. An equal volume of ethanol was added to coagulate the precipitate, and the sample was allowed to stand overnight or longer.

The clear supernatant was decanted as much as possible and the slurry at the bottom was centrifuged in a polypropylene (PP) conical disposable centrifuge tube. The precipitate was dried at <90° C, then dissolved in nitric acid and transferred to Teflon microwave digestion vessels. The concentrated HNO_3 wash contained in the original NIST bottle was also added to the vessels and microwaved to wet acid digest the samples. H_2O_2 and HNO_3 were added during digestion as part of the microwave digestion cycle. The NIST sample bottles were then allowed to dry and were weighed to determine the tare weight.

The clear solution, free of organic compounds, was evaporated to near dryness at low heat and the residue redissolved in 8N HNO_3. Ferrous Ammonium sulfate was added while being warmed and stirred followed by $NaNO_2$ addition. The solution was passed through a conditioned 6 ml of anion exchange (AG1X4) resin, washed with 120 mL of sub-boiled 8N HNO_3 followed by 90 mL of sub-boiled 6N HCl. Plutonium was eluted by 30 mL of sub-boiled 6N HCl-0.1N HI into a tapered-quartz thimble and evaporated to dryness at about 90 degree centigrade.

The next set of procedures were performed inside a class 100 hood. The solution was taken up in 8N HNO_3 and transferred to small conical Teflon vials and again evaporated to dryness at about 90°C. The residue of plutonium was taken up in 100 µL of 4N HNO3 and filtered through 2 µm polypropylene syringe filters into 1 mL conical storage vials.

Item #5:

The samples were aspirated into the mass spectrometer for analysis. A HP4500 ICP-MS was fitted with a micro-concentric nebulizer for sample delivery to the plasma torch. A torch shield was used to minimize the instrument background. The instrument was tuned for maximum sensitivity with a 10 ppb Thallium solution in 2% HNO3. The quadrupole gain was adjusted to center the peak maxima for Pu-239 and 242. An aggregate accumulation time of 108.5 sec was used for each analysis. This process consumed the entire sample.

Item #6: Example calculation made for sample PUR0297-57

ICP-MS Number: MS97-74
Sample ID: PUR0297-57
Sample Mass: 211.3 (gm)
Accumulation period: 108.533 sec

Pu-239 (fg) = [Pu-242 fg]*(C239-B239)/(C242-B242)

for sample PUR0297-57

C239 = 4624 counts at m/e 239
B239 = 315.7 average blank counts at m/e 239
C242 = 8349
B242 = 315.7
Pu-242 = 44.53 fg

Pu-239 = 44.53(4624-315.7)/(8349-315.7)

Pu-239 = 23.88 fg = (23.88 fg) (0.01592 fg/aCi) = 1500 aCi = 55.6 µBq

The concentration is:

[Pu-239] = Activity/sample weight
= 55.6 µBq/0.2113 kg
= 263.0 µBq/kg

The performance curve of observed Pu-239 activity versus the known ratio of Pu-239 to Pu-242, obtained with the results of synthetic urine blanks and spikes, was used to obtain linear regression parameters to evaluate the uncertainty in the sample measurements.

Using this technique, we obtain activity in sample PUR0297-57 1500 +/- 14 aCi at the 1 sigma confidence level.

Expressing these in μBq, we use the conversion factor = 0.037037 μBq/aCi to obtain 55.6 ± 0.5 μBq. For massic activity, divide activities above by corresponding sample mass (211.3 gm in this case) to obtain 263 μBq/kgm.

With the delivery of the results for both fission track and mass spectroscopy analysis we would like to have the actual spike levels for each sample so that we can further evaluate the results. Moreover, these comparisons are necessary for the FY98 program planning, which we are now in the process of formulating and will be reported to DOE within the next several weeks. If there are any questions, please feel free to call either of us at (516) 344-5539 (R. Pietrzak) or (516) 344-2007 (E. Kaplan).

Sincerely yours,

Richard Pietrzak

Richard Pietrzak

Edward Kaplan, Ph.D., Group Leader
Radiological Sciences Division

EK/mcb
encl.

Attachment VI

BNL FTA Report

BROOKHAVEN NATIONAL LABORATORY
ASSOCIATED UNIVERSITIES, INC.
P.O. Box 5000
Upton, New York 11973-5000
TEL (516) 344-2007
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Department of Advanced Technology
Building 703M

May 22, 1997

Dr. Kenneth G.W. Inn
NIST
245/C114
Gaithersburg, MD 20899

Dear Ken:

We are taking the liberty of reporting the results of the samples you recently sent in letter format, rather than using the forms you provided. Please note that the following correspond only to the samples analyzed via the fission track analytical process.

Sample Number	Total Activity in Each Bottle (μBq)	Uncertainty (one sigma)[1] (Lower/Upper) (μBq)	Massic Activity (μBq/kgm)
PUR0297-01	*	*	*
PUR0297-04	2.5	2.2/2.8	11.1
PUR0297-06	0.7	0.4/1.0	3.3
PUR0297-08	1.7	1.4/2.0	7.8
PUR0297-12	27.1	26.8/27.5	123
PUR0297-15	*	*	*
PUR0297-20	23.2	22.9/23.6	100
PUR0297-31	11.4	11.1/11.7	52.5
PUR0297-40	10.0	9.6/10.3	44.9
PUR0297-41	18.2	17.8/18.5	77.6
PUR0297-42	57.0	56.5/57.5	275
PUR0297-50	2.6	2.3/2.9	12.3
PUR0297-51	9.1	8.8/9.4	42.4
PUR0297-53	6.9	6.6/7.2	31.3
PUR0297-59	6.1	5.8/6.4	27
PUR0297-60	3.1	2.8/3.4	14.3
PUR0297-63	2.9	2.5/3.2	12.5
PUR0297-73	48.9	48.5/49.4	237
PUR0297-80	34.1	33.7/34.5	161
PUR0297-83	*	*	*
PUR0297-91	3.2	2.8/3.5	14.1
PUR0297-93	21.6	21.3/22.0	104
PUR0297-96	*	*	*

[1]See explanation for item 6.

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Items below our detection limit (3 sigma of blanks approximately 20-25 aCi, 0.7-0.9 uBq) are indicated with an asterisk. Two samples were lost during processing: sample PUR0297-034 was lost as it was being placed onto the substrate, and sample PUR0297-021 was contaminated with plutonium that was intended for use as a flux monitor. Please note that had we followed our standard protocol, where we process only part of the sample, we would have been able to reanalyze these two lost samples.

Based particularly on our Marshall Islands experience, and as we state in our publications, we are more concerned with false positives than with false negatives. We therefore use this same protocol to reanalyze samples over 10x our detection limit. Unfortunately this was not possible using your instructions. For the same reasons, we also usually report our results at the 99% confidence level, rather than 1 sigma, as you requested.

The following correspond to the items on your reporting forms.

Item #3:

1) Pu standard certification uncertainty: 5%

2) Pu standard preparation error: 3%
(includes dilution error)

3) Thermal neutron flux error: 10%
(includes uncertainty in Pu quantity in the flux)

4) Fission Track counting error: 3%

5) Pu recovery error in the chemistry procedure: 15%

(Three major areas:
1) Co-precipitation step: 5%
2) 1st column separation: 7%, and
3) micro-column separation: 12%)

blank correction = not Constant why? ← 40-60 aCi

Calibration curve:

The calibration curve reflects the sum-total of all the aforementioned errors. An additional uncertainty is the variation found in tracks for synthetic urine (i.e., fission tracks attributable to ^{239}Pu in the reagents and interfering fission tracks from ^{235}U that is also present in the reagents and the process). This uncertainty affects the estimation of ^{239}Pu concentration in samples to a varying degree, that is, it is higher for activity closer to the MDL than it is for activities at the higher end of the calibration region. For example, 70 aCi samples, at the 99% confidence level the error can be about 60%, and at 200 aCi levels, it can be about 30%.

Item #4:

The tapes around the glass NIST sample bottles were removed and the individual weights were noted. The samples were transferred to plastic containers for co-precipitation step. The empty bottles were weighed and noted. To each empty bottle, 5 ml of conc. HNO_3 was added and the acid was sloshed around. They were stored for later addition to the samples. Synthetic urine blanks (a total of seven blanks) and spikes (a total of 16 spikes from 100 aCi to 400 aCi) of equal volume to those of NIST samples were also analyzed along with the samples.

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The pH of each of the sample was adjusted to between 2 and 3 and rhodizonic acid was added to each sample (100 mg for each 100 ml sample) and stirred for 15 minutes. Then pH was adjusted to greater than 9.5 to precipitate calcium rhodizonate that carries plutonium. An equal volume of ethanol was added to coagulate the precipitate, and the sample was allowed to stand overnight or longer.

The clear supernatant was decanted as much as possible and the slurry at the bottom was centrifuged in a polypropylene (PP) conical disposable centrifuge tube. To each centrifuge tube conc. HNO_3 wash contained in the original NIST bottle was added and microwaved for wet acid digestion. H_2O_2 and HNO_3 were added during digestion as part of microwave digestion program.

The clear solution, free of organic compounds, was evaporated to dryness at low heat and the residue re-dissolved in 8N HNO_3. Ferrous ammonium sulfate was added while being warmed and stirred followed by $NaNO_3$ addition. The solution was passed through a conditioned 6 ml of anion exchange (AG1X4) resin, washed with 3 column volumes of sub-boiled 8N HNO_3 followed by 3 volumes of sub-boiled 6N HCl. Plutonium was eluted by 7 column volumes of sub-boiled 6N HCl-0.1N HI into a tapered-quartz thimble and evaporated to dryness at about 90 degree centigrade.

The next set of procedures were performed inside a class 100 hood. The solution is taken up in 8N HNO_3 and passed through a 12 µl micro-column of an anion exchange resin to remove uranium and other ions. Plutonium was eluted in three drops which were collected on a cleaned Suprasil surface, dried under an infrared lamp, packaged under vacuum and irradiated using a thermal neutron fluence of 9E16 n/cm^2.

After irradiation the slides were cleaned and etched in conc. HF for 105 seconds. The enlarged tracks were counted under a microscope.

Item #5:

During fission track counting, a slide was loaded onto a holder and placed on a stage under the magnifying lens of a microscope. As per the flow diagram of attached figures, each Suprasil slide was divided into three equal 1cm^2 areas with each area representing a sample (Right, Center and Left). Each area of 1 cm^2 was further divided into a 24 x 34 (816 frames) matrix to be examined under the microscope. A total magnification of 160 is used. A computer program controls the movement of the stage holding the slide automatically, from the beginning of a row of frames to the end when the stage drops to the next row by one frame and the scanning continues until all 816 frames are completed. During scanning the stage can be stopped for counting the tracks. An average of about 15 to 20 minutes is required for each sample.

Item #6: Example calculation is made for sample PUR0297-08

Fission Track Number: 97-004
Sample ID: PUR0297-08
Sample Mass: 216.5 (gm)
Tracks: 70

Calibration curve using blanks and spikes gives:

$$\text{Tracks} = b_0 + b_1 * (\text{Activity [aCi]})$$

where: $b_0 = 20.47$
$b_1 = 1.08$

For an inverse regression, we obtain (see Eq. [1.7.5] from Draper, N.R. and H. Smith, Applied Regression Analysis, J. Wiley & Sons, 1981, pp 47-51).

$$\left.\begin{matrix} X_U \\ X_L \end{matrix}\right\} = \bar{X} + \frac{b_1(Y_0 - \bar{Y}) \pm ts\{[(Y_0 - \bar{Y})^2/S_{xx}] + (b_1{}^2/n) - (t^2s^2/nS_{xx})\}^{1/2}}{b_1{}^2 - (t^2s^2/S_{xx})}$$

where:

X = activity of a urine sample,
Y = tracks found for a urine sample,
s = variance about the calibration curve,
S_{xx} = sum of squares of residuals of activities in synthetic urine spikes,
t = Student's t-distribution with n-2 degrees of freedom at some specified confidence level,
n = number of synthetic urine blanks and spikes,
X_{bar} = average activity of synthetic urine spikes used in calibration curve,
Y_{bar} = average tracks of synthetic urine blanks and spikes used in calibration curve,

and where 1 + 1/n should be used instead of 1/n to reflect that an individual observation is being used (instead of a population mean).

Using this equation, we obtain activity in sample PUR0297-08 of 46 ± 9 aCi at the 1 sigma confidence level.

Expressing these in uBq, we use the conversion factor= 0.037037 uBq/aCi to obtain 1.7 ± 0.3 uBq. For massic activity, divide the activity by the sample mass (216.5 gm) to obtain 7.8 uBq/kgm.

As I mentioned in our recent phone conversation, and as confirmed with Neil Barss (DOE/EH-63), we expect to report results using ICPMS by May 30th.

Very truly yours,

Anant R. Moorthy

Anant Moorthy, Ph.D.

Edward Kaplan, Ph.D., Group Leader
Radiological Sciences Division

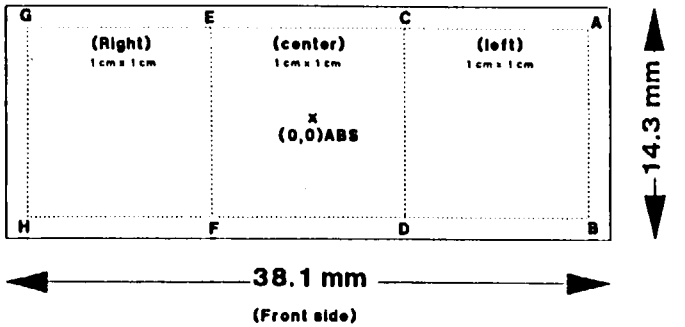
EK/jk
encl.

Figure 1

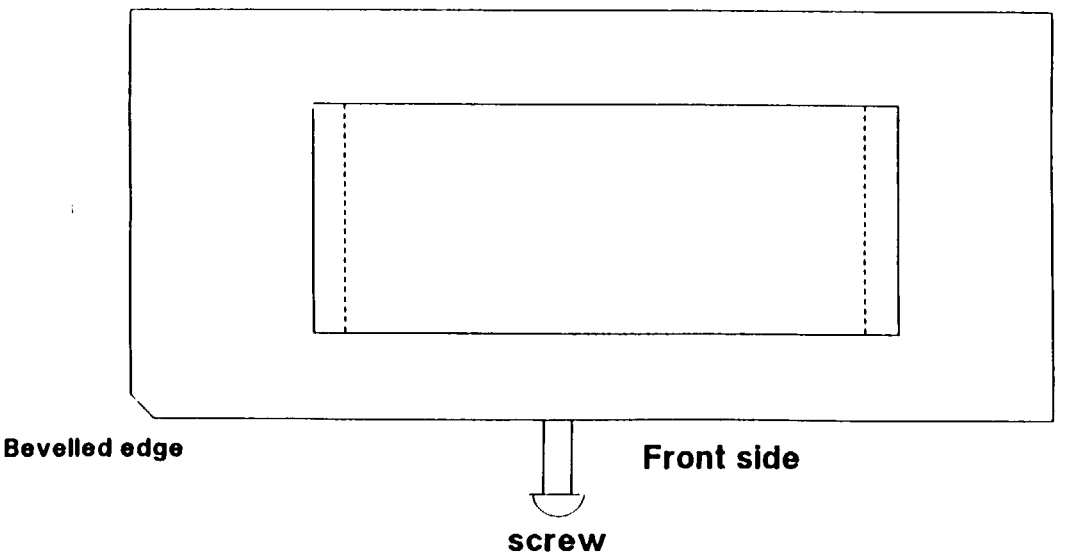
Slide and slide holder

(not to scale)

1) slide (quartz)



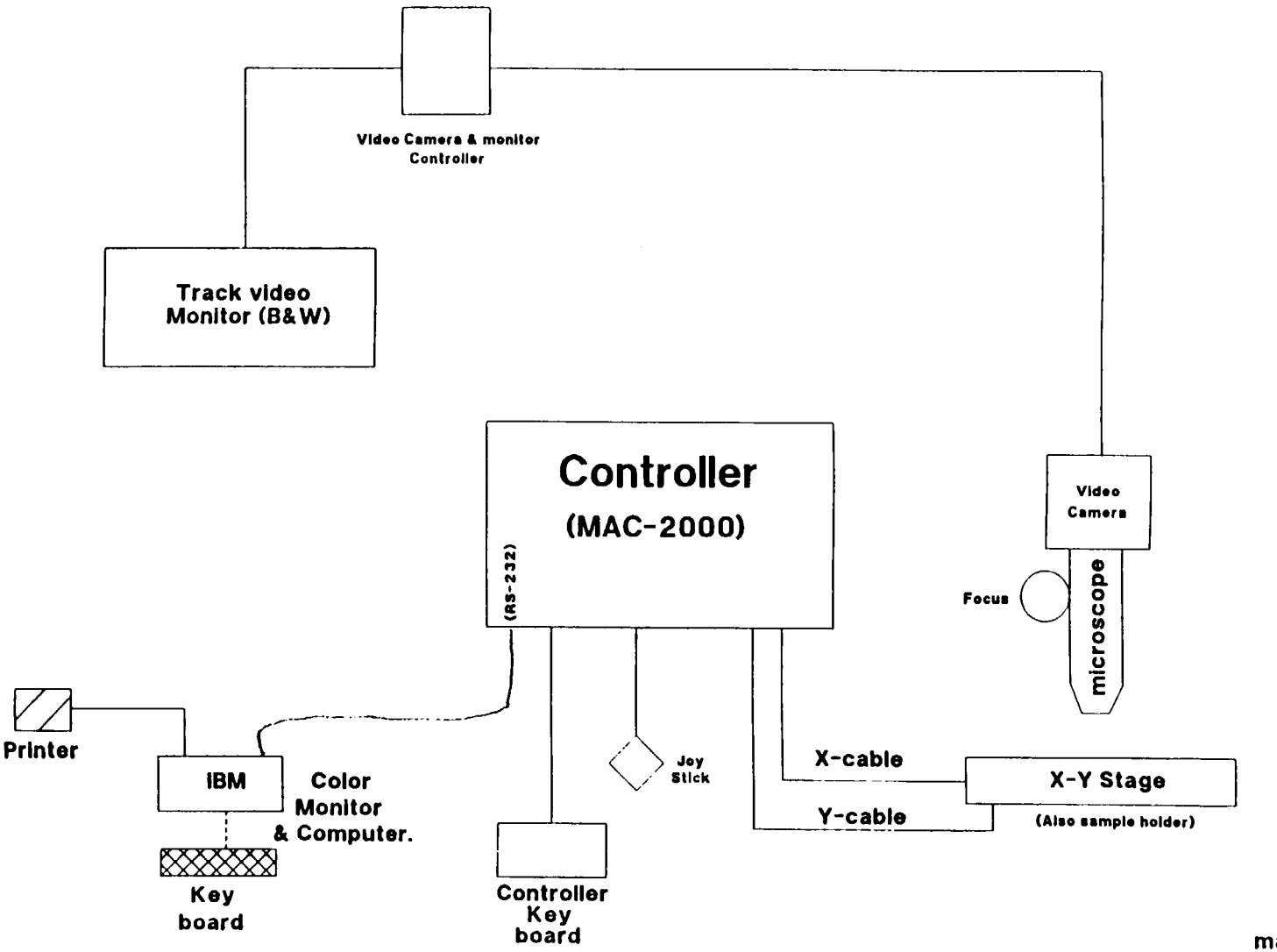
2) Slide Holder (aluminum)



sld&hldr.drw
05/09/93

Figure 2

FISSION TRACK COUNTING SET-UP



macsetup.drw

Attachment VII

LANL TIMS Report

UNCLASSIFIED FACSIMILE

LOS ALAMOS NATIONAL LABORATORY
ANALYTICAL QUALITY AND CHEMICAL INFORMATION MANAGEMENT
(CST-3)
P.O. BOX 1663, MS K484
LOS ALAMOS, NM 87545
FAX NO: (505) 665-5982
CONFIRMATION NUMBER: (505) 665-7323

TOTAL PAGES (INCLUDING COVER SHEET): 15

DATE: 5-13-97

FROM: Peggy Gautier PHONE: 505-667-6235

TO: Kenneth G.W. Inn FAX NO: 301-869-7682

TO: _____ FAX NO: _____

TO: _____ FAX NO: _____

SUBJECT: "Results of Measurement 239/240 Pu in Artificial Urine"

COMMENTS: hard copy to follow in overnight mail.

OPERATOR: Carolyn J. Macdonell

Results of Measurement of $^{239/240}Pu$ in Artifical Urine
Los Alamos National Laboratory

Contact Person: Moses Attrep, Jr. (505) 667-0088

1. Please use this data reporting form for the submission of analytical results. Twenty-five samples of $^{239/240}Pu$ spiked unstable artifical urine (<10,000 aCi/sample) have been provided for this study. Please analyze the total content of each bottle of sample, and report the individual measurement results. The reference date and time for your reported results are:

12:00 noon EST, February 26, 1997

2. Report measurement in $Bq{\cdot}g^{-1}$ of solution. Report total combined standard uncertainty as 1s (%).

Table I. Los Alamos National Laboratory Results for Plutonium Samples.

YANKEE ATOMIC ID PUR0297	Sample Number (LANL)	Total Activity (Bq) in Each Bottle	Massic Activity ($Bq{\cdot}g^{-1}$)	Uncertainty (% 1s)
05	00.35866	7.40 E-05	3.30E-07	8.2
09	00.35867	4.77 E-05	2.23 E-07	12.2
11	00.35868	2.78 E-05	1.28 E-07	17.6
13	00.35869	2.31 E-05	1.09 E-07	19.4
19	00.35870	3.62 E-05	1.76 E-07	17.1
21	00.35871	7.45 E-05*	3.44 E-07*	10.9
22	00.35872	2.23 E-05	1.01 E-07	22.5
25	00.35873	1.90 E-05	8.44 E-08	35.5
27	00.35874	5.44 E-05	2.54 E-07	8.7
37	00.35875	6.45 E-06	2.93 E-08	70.2
39	00.35876	1.55 E-05	7.12 E-08	32.9
45	00.35877	8.83 E-06	3.97 E-08	58.4
47	00.35878	1.76 E-05	7.94 E-08	28.5
48	00.35879	6.90 E-06	3.19 E-08	66.7
61	00.35880	2.34 E-06	1.08 E-08	184.3
66	00.35881	7.83 E-06	3.59 E-08	59.5
68	00.35882	-1.78 E-06*	-8.84 E-09*	249.1
77	00.35883	2.83 E-05	1.45 E-07	31.6
78	00.35884	1.68 E-05*	8.26 E-08*	28.7
82	00.35885	6.99 E-06	3.13 E-08	78.2
86	00.35886	-2.31 E-06	-1.11 E-08	195.4
89	00.35887	1.28 E-05	5.90 E-08	37.2
90	00.35888	1.15 E-05	5.60 E-08	39.0
95	00.35889	1.09 E-04*	4.92 E-07*	13.9
98	00.35890	-1.49 E-06	-7.14 E-09	294.4

*Upper limit

3. The ±1s "standard uncertainty" components (random and systematic) which comprise the combined standard uncertainty. These may include, but not limited to the following:

Uncertainty due to calibration factor/efficiency:	NA
Uncertainty due to dilutions/source preparation :	NA
Uncertainty due to impurity corrections :	ND
Uncertainty due to tracer calibration :	0.25%
Uncertainty due to gravimetric measurements :	~0.1%
Uncertainty due to spectral interferences :	~0.1%
Others, please describe.	

The errors reported for these results are reflective of the uncertainties of the thermal ionization measurements. These uncertainties are larger than the uncertainties due to other measurements (weighing, etc.) stated above.

4. Describe in detail how the TEST samples were used, (i.e., give a detailed chronological description of the handling of the samples from the time they were opened to the time of reporting of results). This should include a description of solution transfer methodologies, chemical yield tracer additions, chemical separation used, measurement source preparation, storage of samples, etc. **Please attach a separate page if necessary.**

Note: The procedures and other information are included in the report and are not placed on separate pages.

The standard procedure for plutonium bioassay samples at Los Alamos National Laboratory was used for these samples. This included (a) preparation for alpha counting, (b) stripping off disc and preparation for TIMS, and (c) TIMS analysis and data reduction. This includes a calcium phosphate precipitation and a nitric acid column purification before electro deposition and counting. Following counting the plutonium is stripped from the discs and purified by two columns before TIMS preparation and instrumental analysis.

1.0 Removing Sample from Bottles

1.1 The samples were logged into the sample management system and stored at ~4° C until they were delivered to TA-48 for processing. Upon arrival at TA-48, RC-45, our clean room facility, the samples were stored in a refrigerator at ~4° C until processing commenced.

1.2 Sets of 12 samples which included QA samples and process blanks were taken to the first laboratory for initial processing. The outer plastic cover was removed and the lids were unscrewed to allow the pressure in the bottles to come to our atmospheric pressure and the lids were rescrewed.

1.3 The samples were then weighed on a single pan balance (± 0.3 g). From each sample 0.5 mL was removed for making a specific gravity measurement. The bottle was then reweighed. The contents of the bottle were then delivered

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into a new, clean 400 mL beaker. The bottle was then rinsed three times with approximately 3 mL of 8 M HNO_3 and the contents added to the beaker. The bottle and cap was then rinsed with water and allowed to dry before being reweighed. The amount of sample was determined from the weighings.

2.0 Radiochemical Purification Procedure

2.1. *Preparation of 500 g of Bio-Rad AG 1-X4, 100-200 mesh resin for the anion exchange of plutonium.*

2.1.1. To remove the fines, pour 500 g of resin into a 2-L beaker and add water to give a volume of approximately 1600 mL.

2.1.2. Stir the slurry on a magnetic stirrer for 20 min.

2.1.3. Slowly decant the water along with the fines when the bulk of the resin settled.

2.1.4. Repeat Steps 2.1.1 to 2.1.3 two using 8 M HNO_3 instead of water. A final rinse is made with water.

2.1.5. Store the resin slurry in the orginal bottle in water.

2.2. *Chemical separation of plutonium in sample.*

2.2.1. Add 5 to 10 drops of 1-octanol to the sample if sample is foamy.

2.2.2. Add 1.0 mL of the ^{242}Pu tracer solution.

2.2.3. Add 200 µL of $Ca(NO_3)_2$ solution.

2.2.4. Add 1 mL of concentrated H_3PO_4.

2.2.5. Add 10 mL of 30% H_2O_2.

2.2.6. Add 100 mL of conc NH_4OH.

2.2.7. Cover the beakers with Parafilm™ and let samples precipitate overnight.

2.2.8. Remove the Parafilm™ and decant if the solution is clear.

2.2.9. Pour the remaining slurry into a 250-mL Teflon bottle. Screw cap on.

2.2.10. Centrifuge for 5 min.

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2.2.11. Remove cap and pour off supernatant solution.

2.2.12. Add an equal amount of conc HNO_3 to the precipitate slurry and cap loosely. Swirl to dissolve particles adhering to the surface of the bottle.

2.2.13. Add 75 mL of 8 M HNO_3 to the bottle. Heat on the hot plate that has a surface temperature of 120-150° C for 1.5 hours.

2.2.14. Cover samples and transfer to clean room. move to clean room

2.3. *Anion exchange separation.*

2.3.1. Put a plug of glass wool into the bottom of the anion exchange column and fill the column with AG 1-X4, anion exchange resin to a height of 6-7 cm. Wash the column with H_20 until the resin column maintains a constant level.

2.3.2. Wash the column reservoir with 75 mL of 8 M HNO_3 and allow the solution to pass through the column. Discard the eluent.

2.3.3. Pour the sample into the column reservoir.

2.3.4. When all of the sample has been transferred to the column reservoir and has completely drained, rinse the bottle with 8 M HNO_3 and pour the washings into the column reservoir. Wash the bottle two additional times with 5-10 mL 8 M HNO_3.

2.3.5. When the 8 M HNO_3 solution has drained, wash the walls of the reservoir with 8 M HNO_3. Repeat this washing three additional times.

2.3.6. Fill the reservoir with 75 mL of 8 M HNO_3, drain down to the top of the column.

2.3.7. Place a 100-mL beaker under the column after all the wash solution has flowed through the column.

2.3.8. Add 2 mL of 5% $NaHSO_4$ solution to the 100-mL beaker.

2.3.9. Add 25 mL of 0.36 M HCl-0.01 M HF eluting solution to the column.

2.3.10. Collect the effluent in the beaker containing the 5% $NaHSO_4$. Evaporate the slurry to dryness on a hot plate with a surface temperature of 120-150°C for the first 30 min because the solution may splatter. After the sample has been dried, add 5 mL concentrated HNO_3 and 1 mL of 30% H_2O_2. Take to dryness on the hot plate. Repeat HNO_3-H_2O_2 treatment, if necessary.

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2.3.11. Remove beaker from hot plate and allow to cool.

2.4. *Electrodeposition.*

2.4.1. Add 4 mL of the electrolyte solution (15% Na_2SO_4) to the beaker and allow to set for 20-30 minutes.

2.4.2. Engrave back of stainless steel disc with sample numbers.

2.4.3. Assemble the cell, placing the disk into the bottom depression of the cap, and screw together.

2.4.4. Fill the cell with water to test for leaks. Discard the water.

2.4.5. Add the sample solution to the cell.

2.4.6. Rinse the sample beaker with water and add the wash to the cell. Fill the cell with water to within 14 mm of the top of cell.

2.4.7. Place the cell in the electrodeposition rack so that the platinum wire electrode is inserted into the cell . The bottom of the platinum electrode is 12 mm from the stainless steel disc.

2.4.8. Attach the cathode lead to the cell cap.

2.4.9. Turn on the main switch of the electrodeposition unit. Set current to 0.5 amps.

2.4.10. Electroplate for 180 min.

2.4.11. Add 1 to 2 mL of 25% NaOH to the cell and after 60 seconds turn off the current.

2.4.12. Pour the solution out of the cell and disassemble the cell. Wash the stainless steel disc with H_20. Be sure not to touch the surface of the disc.

2.4.13. Dry the disk in the coin holder on the hot plate set on "low"; label coin holders with sample identification.

2.5. Samples are delivered to count room for a 70,000 sec alpha count. Following counting, the samples are returned to clean room for processing for thermal ionization mass spectrometry analysis.

2.6. *Strip from Stainless Steel Discs and Final Anion Columns for Bioassay Samples.*

2.6.1. Place the stainless steel disc on top of an inverted 50 mL Teflon beaker. Add 2 drops of conc HF and evaporate to dryness under a heat lamp. Add 2 drops of conc HNO_3 to the disc and evaporate to dryness.

2.6.2. Rinse the plutonium from the disc with conc HNO_3 into a 40 mL centrifuge tube. Evaporate the nitric acid solution containing the plutonium to dryness.

2.6.3. A Poly-Prep™ chromatography column (Bio-Rad) is filled to the 1.8 mL level with AG MP-1, 50-100 mesh, anion exchange resin. The resin is conditioned with three 2 mL additions of 8 M HNO_3.

2.6.4. The sample is taken up using 2 mL of 8 M HNO_3 and loaded onto the column. The sample tube is washed with two 1-mL additions of 8 M HNO_3 and the wash is added to the column allowing the solution to drain completely between each addition. Finally, the column is rinsed with three 2-mL additions of the 8 M HNO_3.

2.6.5. A clean centrifuge tube is placed under the column and the plutonium is eluted by adding three 1.5-mL additions of 0.5 M HCl followed by three 2 mL additions of the HI-HCl reagent (1:9 ratio, by volume HI to HCl).

2.6.6. The sample is evaporated to dryness. One mL of conc HNO_3 is added and the sample is evaporated to dryness again. Finally 1 mL of conc HCl is added and the sample is taken to dryness.

2.6.7. A small anion exchange chromatography column is prepared by placing AG MP-1, 50-100 mesh resin in a disposable pipette tip that is 7-cm in length by 5-mm in diameter. Prewashed quartz wool plug is inserted in the pipette tip and resin is added to a depth of 2 cm.

2.6.8. The column is conditioned with two 1-mL additions of a H_2O_2-HCl reagent (2 drops of 30% H_2O_2 to 10 mL conc HCl) that is freshly prepared.

2.6.9. The sample is dissolved with 1 mL of the H_2O_2-HCl solution and loaded onto the column. The sample tube is washed with two 1-mL additions of the H_2O_2-HCl solution and added to the column.

2.6.10. The column is rinsed with four 0.75-mL additions of 8 M HNO_3. The solution is allowed to drain completely each time before adding the next rinse.

2.6.11. The plutonium is eluted from the column into clean 10 mL quartz test tubes using three 0.75-mL additions of conc HBr. Each addition is allowed to drain completely before adding the next. — Stop up no quality

2.6.12. The HBr is evaporated to dryness.

S4/

2.6.13. Seven drops of conc HNO_3 and 7 drops of conc $HClO_4$ are added to each sample and heated at 180° C until dry in a heat block. The sample is cooled to room temperature and 10 drops of conc HCl are added. The sample is slowly evaporated in a heat block until dry.

2.6.14. The samples are submitted for mass spectrometric analysis.

2.7. *Thermal Ionization Mass Spectrometric Filament Preparation.*

The mounting of the previously purified plutonium sample is accomplished by electrodeposition of the plutonium with a small quantity of platinum. A larger quantity of platinum is then electrodeposited over the plutonium to provide a diffusion barrier which dissociates plutonium molecular species and provides high ionization efficiency.

2.7.1. The electrodeposition apparatus is assembled with parts that have been cleaned and stored in the clean room.

2.7.2. One hundred µL of 1.5 M NH_4Cl (buffered to pH 2.8 with pure ammonia gas) and 10 µL of 1.5 M HCl are added to the quart tube containing the chemically purified plutonium sample.

2.7.3. The solution is warmed with a heat lamp for 2 minutes and 5 µL of DNS (dihydrogen dinitrosulfatoplatinate (II), 2 µg/mL in 1.5 M HCl) is added.

2.7.4. The solution is transferred with a transfer pipette to the filament on the electrodeposition apparatus and electrolyzed for 20 minutes at 3.4 V.

2.7.5. The voltage is reduced to 3.0 V and 5 µL of platinum DNS (5 µg/mL) is added.

2.7.6. Electrolysis is continued for 20 minutes at 3.0 V.

2.7.7. With the plating voltage on at 3.0 V, the electrolyte is rinsed from the filament with deionized water.

2.7.8. The filament is removed from the plating apparatus and rinsed thoroughly with deionized water and finally with glass distilled acetone. — higher purity

2.7.9. The filament is first dried under a heat lamp for 10 minutes. The filament is then resistively heated to 350° C by running 1.25 amps current through the filament for 5 minutes while the heat lamp is still on.

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2.7.10. The filament is placed into the filament carrier for insertion into the mass spectrometer as quickly as possible to prevent reabsorption of water onto the filament.

2.7.11. The mass spectrometer with the loaded samples is pumped down to a pressure of 1-2 x 10^{-6} torr in the source chamber and 2-4 x 10^{-9} torr in the analyzer.

2.7.12. The heating protocol for analysis of plutonium is as follows:

Table II. Heating Protocol for TIMS Analysis.

Approximate Time (Minutes)	Approximate Filament Temperature (°C)	Comments
0	1100	
2	1200	
4	1300	
6	1400	Begin search for ^{242}Pu peak
8	1450	Optimize ion source
10	1500	Instrument is tuned
12	1550	Start base line acquisition on bases of interest
20	1580	Data acquisition
30	1580	Data acquisition
60	1580+	Data acquisition should be complete

5. Describe the type of measurement system used, including a general description of its operation. Also indicate the type of analysis software utilized for any calculations and/or corrections applied to raw measurement data if applicable.

1.0. **TIMS Data Collection**

Measurements are made on a single stage thermal ionization mass spectrometer which is housed in our clean room facilities. The end of the previous section describes the preparation of the sample before making measurements.

The following is a description of the protocol used for collecting data for the plutonium bioassay samples. The bioassay samples require the precise measurement of the plutonium isotope in the samples. The primary plutonium isotopes measured are ^{239}Pu and ^{240}Pu. When the signal or amount of ^{239}Pu is very low, it is not reasonable to spend time in trying to measure the ^{240}Pu. The

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amount of ^{239}Pu is always larger than the amount of ^{240}Pu. This is reflected in the protocol that has been established for these measurements.

Baseline are run in all cases. Measurements will commence when the ^{242}Pu (the tracer) count rate exceeds 50,000 counts per second. Upper limit measurements for $^{239}Pu/^{242}Pu$ ratio will continue until the 242.5 mass count rate falls below 1.5 counts per second. Real measurements will commence at that point.

If the $^{239}Pu/^{242}Pu$ ratio is 3×10^{-5} or greater, the protocol will dictate a time symmetric measurement sequence: 1 block of $^{239}Pu/^{242}Pu$, 2 blocks of $^{240}Pu/^{242}Pu$, and two blocks of $^{239}Pu/^{242}Pu$. Typical collections of data to create a block are given in figures 1 and 2.

If the $^{239}Pu/^{242}Pu$ is less than 3×10^{-5}, then usually 4-5 blocks of $^{239}Pu/^{242}Pu$ will be taken.

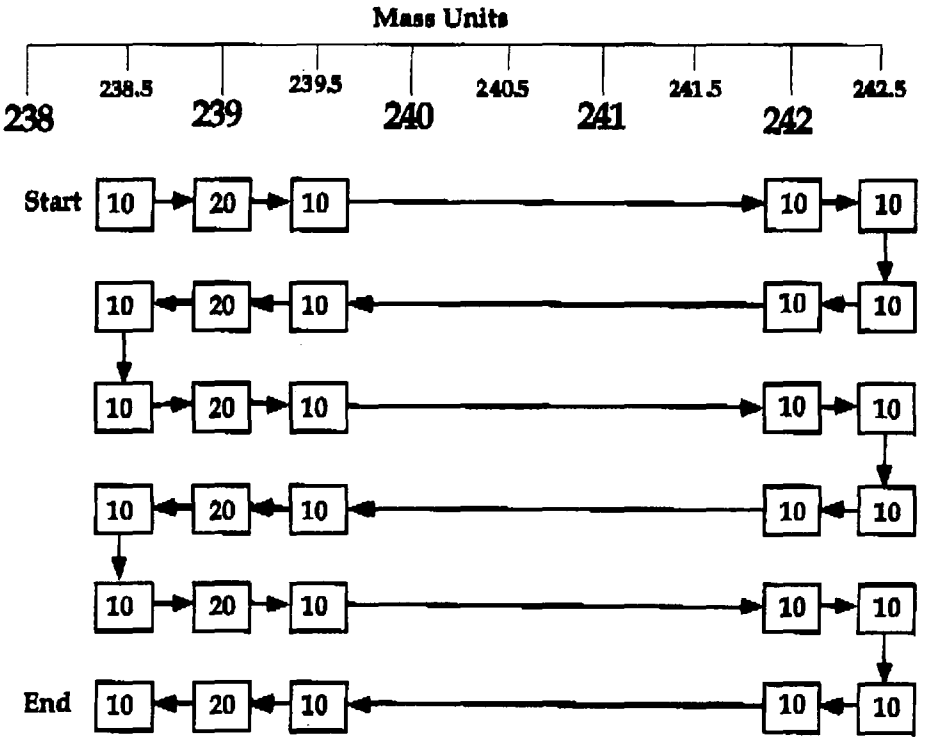

Figure 1. Measurement Sequence for Acquiring One Block of 239/242 Data.

Typical Sequence of Mass Spectrometric Measurements if 242/239 ratio is less than 3×10^{-5}. Numbers in blocks are typical 1-second counts at that mass region. The number of 1-second counts may vary.

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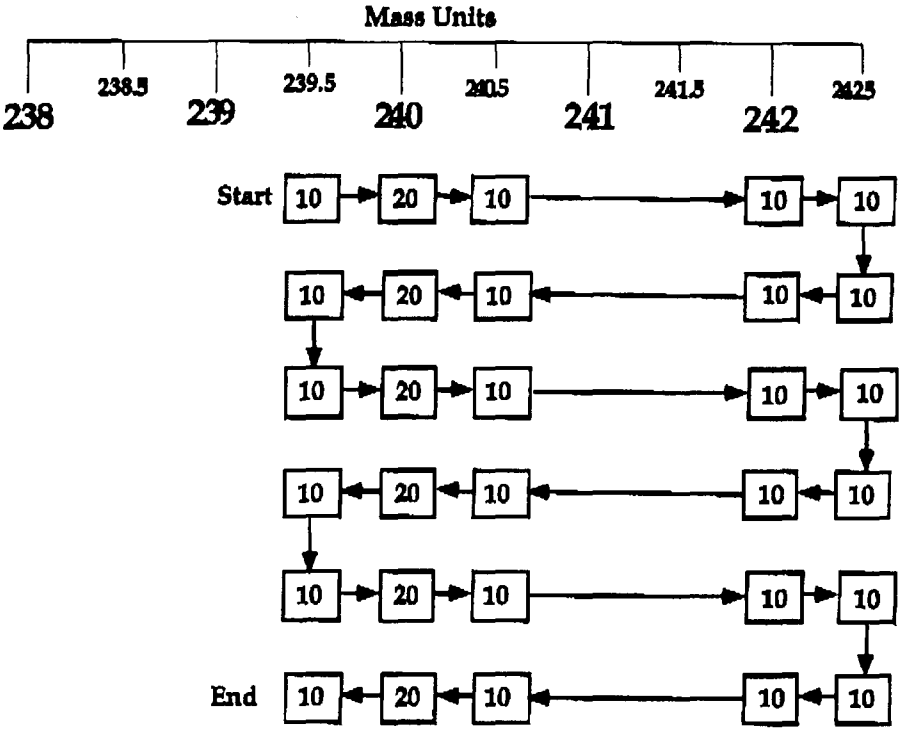

Figure 2. Measurement Sequence for Acquiring One Block of 240/242 Data.

Typical Sequence of Mass Spectrometric Measurements if 242/239 ratio is greater than 3×10^{-5}. Numbers in block are typical 1-second counts at that mass region.

6. Using actual measurement data, calibration factors, corrections, etc., give a sample calculation showing how the massic activity and uncertainty values reported in section 2 were determined. Indentify all values used, e.g., efficiency, calibration factors, mass, volume, decay corrections, etc.). **Attach a separate sheet if necessary.**

1.0. TIMS Data Treatment

The following example is given for a bioassay sample calculation. Because the actual spreadsheets and calculations are extensive only pertinent portions of it are given to illustrate the steps of the calculations and associated statistics involved in the TIMS calculations.

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This is not one of the samples reported in this report.

The count rates taken in each block are averaged and the background counts are subtracted. Five blocks of data are represented in Table I where the data are treated with regards to acceptance.

1.1. Column 1. These are the $^{239}Pu/^{242}Pu$ ratios that have the backgrounds subtracted.

1.2. Column 2. This column has the corresponding standard deviations (SD) of the measured $^{239}Pu/^{242}Pu$ ratios.

1.3. Column 3. The ratio divided by the standard deviation (SD) squared is the first element in determining a weighted average.

1.4. Column 4. The value $1/SD^2$ is the weighting factor used for calculating the weighted average given at the bottom of the table with its standard deviation.

1.5. Column 5. The value of the [(average value - individual value)/SD]2 is for the determined the reduced Chi Square value. This is determined as 1.836. The expected Chi Square value is 1.140. If the determined Chi Square value were 1.140 or less, then the all the data would be accepted with the average and standard deviation. Since this set of data does not meet this criterion, Chauvent's Criterion for rejection of data is used.

1.6. Column 6 through 10 are for the purpose of determining which data points may be rejected using the Chauvenet's Criterion.

1.7. Column 6. Starting at the bottom of column one the average of the last two samples are made and reported at the bottom of column 6. The average in the box above is for the three last entries. This is repeated until the top number is the average of all the values.

1.8. Column 7. The corresponding standard deviations are given in this column.

1.9. Column 8. This is the number of standard deviations the measured 239Pu/242Pu ratio varies from the ascending average.

1.10. Column 9. These are calculated Chauvenet's Criterion values.

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Table III. One Block of TIMS Data for $^{239}Pu/^{242}Pu$ Ratio.

Column 1	Column 2	Column 3	Column 4	Column 5	Column 6	Column 7	Column 8	Column 9	Column 10	
239/242 Ratio	Std Dev	X/SD^2	1/SD^2	(Ave-X/SD)^2	Ascending Average	Ascending SD	Number of SD	Chauvenet's Criterion	All Positive OK	
2.6777E-05	5.0859E-06	1.035E+06	3.866E+10	8.494E+00	1.370E-05	5.179E-06	-2.525	2.128	-0.397	
2.4674E-05	4.2628E-06	1.358E+06	5.503E+10	8.903E+00	1.277E-05	3.846E-06	-3.095	2.100	-0.995	Delete Point
1.4801E-05	2.8362E-06	1.840E+06	1.243E+11	1.007E+00	1.185E-05	1.819E-06	-1.621	2.070	0.449	
1.4079E-05	2.8934E-06	1.682E+06	1.195E+11	5.394E-01	1.161E-05	1.659E-06	-1.490	2.038	0.548	
1.3400E-05	2.3111E-06	2.509E+06	1.872E+11	3.911E-01	1.138E-05	1.537E-06	-1.312	2.002	0.690	
1.2322E-05	2.4823E-06	2.000E+06	1.623E+11	2.199E-02	1.118E-05	1.459E-06	-0.783	1.960	1.177	
1.2519E-05	2.5664E-06	1.901E+06	1.518E+11	4.843E-02	1.105E-05	1.487E-06	-0.985	1.914	0.929	
1.2850E-05	1.9396E-06	3.415E+06	2.658E+11	2.132E-01	1.087E-05	1.478E-06	-1.339	1.863	0.524	
9.3390E-06	1.9457E-06	2.467E+06	2.641E+11	1.807E+00	1.059E-05	1.342E-06	0.931	1.803	0.872	
9.2945E-06	2.1414E-06	2.027E+06	2.181E+11	1.543E+00	1.080E-05	1.341E-06	1.120	1.731	0.611	
1.1675E-05	1.9830E-06	2.969E+06	2.543E+11	1.983E-02	1.110E-05	1.253E-06	-0.462	1.645	1.183	
1.0154E-05	2.1013E-06	2.300E+06	2.265E+11	7.336E-01	1.095E-05	1.398E-06	0.570	1.534	0.964	
1.2856E-05	2.3905E-06	2.250E+06	1.750E+11	1.424E-01	1.122E-05	1.583E-06	-1.085	1.383	0.348	
1.1100E-05	2.0508E-06	2.639E+06	2.378E+11	1.734E-01	1.040E-05	9.931E-07	-0.707	1.150	0.443	
9.6959E-06	1.7467E-06	3.178E+06	3.278E+11	1.672E+00						
		Σ = 3.357E+07	Σ = 2.808E+12	Reduced Chi^2						
				1.836						
				Expected Value						
				1.140						

1.11. Column 10. The values in this column represent the difference of column 9, Chauvenet's Criterion and the absolute value of the number of standard deviations of column 8. The test has been constructed so that all negative values may be rejected. The "Deletion Point" is noted on the last negative value.

The data points are seen graphed in Figure 3.

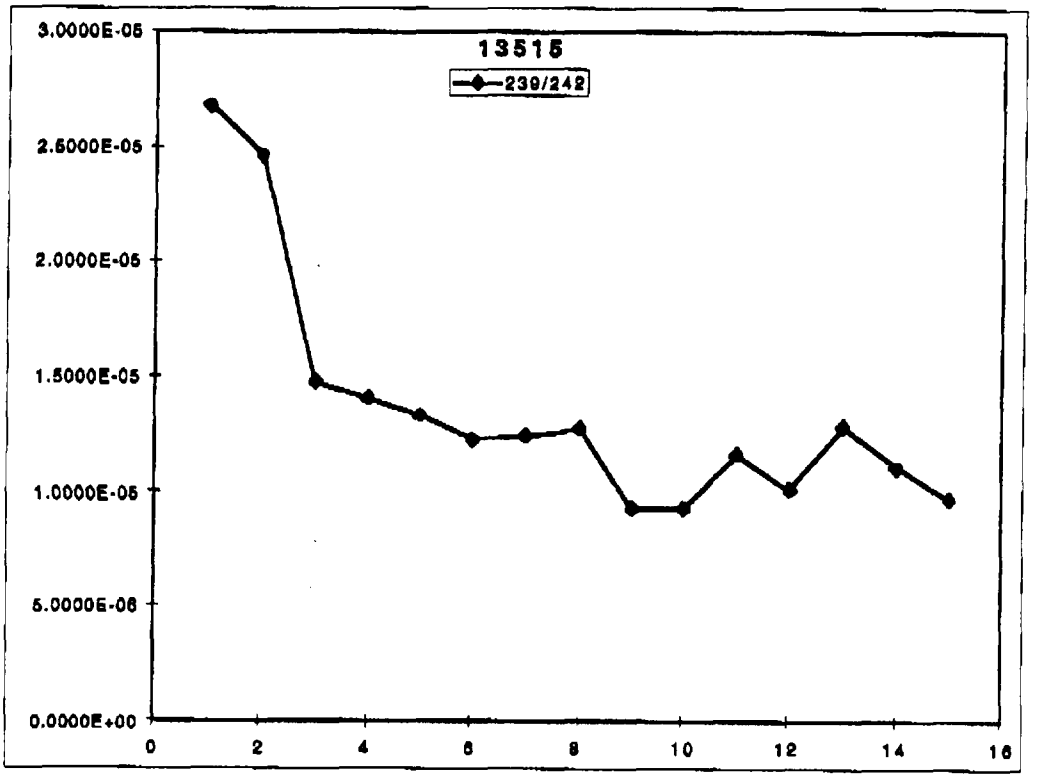

Figure 3. Plot of individual $^{239}Pu/^{242}Pu$ values.

1.12. The process of calculating the weighted average is repeated with the first two points rejected. As expected the reduced Chi Square is 0.643 for the set of data and the expected value is 1.148. This yields an average of $1.149 \times 10^{-5} \pm 6.067 \times 10^{-7}$ (% SD = 5.28%), for this example.

1.13. The sample is then corrected for mass fraction (0.0011) yielding a mass corrected value of $1.145 \times 10^{-5} \pm 6.067 \times 10^{-7}$ (5.28%).

1.14. Process blank contribution to the ^{239}Pu is subtracted:
$(1.145 \times 10^{-5} \pm 6.067 \times 10^{-7}) - (1.644 \times 10^{-7} \pm 2.154 \times 10^{-7}) = 1.129 \times 10^{-5} \pm 6.565 \times 10^{-5}$.

↑ measurement precision + Process BLK correction

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1.15. The amount of tracer added at the beginning of the experiment was 1.050 g which contained 7.5245×10^{12} atoms ^{242}Pu per gram of tracer. Uncertainty in this value is 0.25% and is not propogated in this calculation. Exactly 1.050 g solution was added initially. There are 7.5245×10^{12} atoms ^{242}Pu per g solution; this is 7.901×10^{12} atoms ^{242}Pu added.

1.16. The number of ^{239}Pu atoms in the sample initially is: $(1.129 \times 10^{-5} \pm 6.565 \times 10^{-7}$ atoms $^{239}Pu/^{242}Pu) \times (7.901 \times 10^{12}$ atom $^{242}Pu) = 8.920 \times 10^{7} \pm 5.191 \times 10^{6}$ atoms ^{239}Pu in the sample measured.

1.17. The half-life used for ^{239}Pu is 2.410×10^{4} years. The decay constant, λ, in sec^{-1} is 9.118×10^{-13}. The number of Bq in the sample measured is 9.118×10^{-13} $sec^{-1} \times 8.922 \times 10^{7} \pm 5.191 \times 10^{6}$ atoms $= 8.133 \times 10^{-5} \pm 4.734 \times 10^{-6}$ Bq in the sample measured.

1.18. Remembering that the sample had 0.5 mL removed for a specific gravity measurement, the correction for the activity in the sample as received is $8.133 \times 10^{-5} \pm 4.734 \times 10^{-6}$ Bq x (225.2 g as received/224.7 g sample measured) = $8.151 \times 10^{-5} \pm 4.745 \times 10^{-6}$ Bq in sample as received.

1.19. The amount of Bq/g sample is $(8.151 \times 10^{-5} \pm 4.745 \times 10^{-6})$ Bq/225.2 g = $3.619 \times 10^{-8} \pm 2.107 \times 10^{-9}$ Bq/g sample.

1.12. The values reported with 3 significant figures would be:

Total Activity in the Bottle:	8.13 x 10-5 Bq
Massic Activity:	3.62 x 10-8 Bq/g sample
Uncertainty:	5.82% (1s)

— measurement precision + process Bulk

7. The deadline for submitted report is May 9, 1997. Please address results and technical questions to:

Kenneth G.W. Inn
NIST
245/C114
Gaithersburg, MD 20899

Phone: 301-975-5541
Fax: 301-869-7682
email: kenneth.inn@nist.gov

62

Donivan Porterfield, 01:38 PM 6/1/97 -, assessment of ORNL low-level

X-Sender: dporterfield@lims1.lanl.gov (Unverified)
Date: Sun, 01 Jun 1997 13:38:34 -0600
To: kenneth.inn@nist.gov
From: "Donivan Porterfield, LANL CST-3" <dporterfield@lanl.gov>
Subject: assessment of ORNL low-level Pu in urine PE samples

Pat Brug requested that I send you this draft memo regarding our results from the special low-level plutonium in urine samples from ORNL.

The attached file should be in MS Word 6.0.
Attachment Converted: C:\EUDORA\ENCL\CST-ACES.doc

Donivan Porterfield (505) 667-4710
Los Alamos National Laboratory (505) 665-5982 fax
MS K484, CST-3 (Analytical Quality and Chemical Information Management)
Los Alamos, NM 87545 dporterfield@lanl.gov

To: Distribution
From: Donivan Porterfield, CST-3
Thru: Peggy Gautier, CST-3
Date: DRAFT (5/25/97)

Re: Summary of results from ORNL low-level plutonium in urine pilot study

CST Analytical Chemistry has participated in the Oak Ridge National Laboratory (ORNL) Bioassay Intercomparison study for several years. With the transition of routine plutonium in urine bioassay analyses from CST-9/TA-59 to CST-11/TA-48 CST-3 has continued the participation of Analytical Chemistry in this study. Three study samples are supplied on a quarterly basis for the following analytes and matrices and distributed as indicated:

Analyte	Matrix	Capability
Americium-241	Urine	CST-9/TA-59
Plutonium	Urine	CST-11/TA-48
Plutonium	Urine	CST-9/TA-59
Strontrium-90	Urine	CST-9/TA-59
Total Uranium	Urine	CST-9/TA-59
Tritium	Urine	CST-9/TA-59

With the addition of the thermal ionization mass spectrometry (TIMS) capability, ORNL suggested that they could supply us with a similar plutonium in urine samples but at a lower plutonium spike level. As a pilot ORNL offered to provide several samples of this type at no charge. This offer was accepted and ORNL prepared and shipped these samples to CST-3 for submission to CST-11 for analysis by alpha spectroscopy and TIMS. This memo is to report the results of the analysis of these supplied samples and invite input in the decision to participate on a regular basis in a low-level ORNL intercomparison study.

The reported results will be assessed on the basis of relative bias and relative precision as indicated in ANSI 13.30 (*Performance Criteria for Radiobioassay*), sections 4.3.2 and 4.3.3. These sections provide performance criteria of -0.25 to $+0.50$ for relative bias and <0.4 for relative precision.

The samples supplied by ORNL will be referenced with the CST-AC sample number since the ORNL sample identification used personal identification of the urine donors. In addition to the four samples provided that were spiked with plutonium-239 there were two samples spiked with plutonium-238. Since the plutonium activity of these samples was below that detectable by alpha spectroscopy and TIMS doesn't report plutonium-238 these results will not be evaluated in this memo. As well, since the plutonium-239 activity of this plutonium-238 spike is unknown, the plutonium-239 results for these two samples will not be assessed.

Plutonium-239 by TIMS

Sample ID	Known (aCi/sample)	Reported (aCi/sample)	Bias	Relative Bias	Relative Precision
97.01029	3040	3234	0.064		
97.01030	3070	4258	0.387		
				0.225	0.229
97.01033	12200	12490	0.024		
97.01034	12200	12700	0.041		
				0.032	0.012
			Overall	0.129	0.173

As indicated above all relative bias and relative precision values meet ANSI 13.30 acceptance criteria at the indicated spike levels.

On the basis of these results, ORNL feels assured in their ability to provide low-level plutonium in urine intercomparison samples. However, they have also indicated that they would not be comfortable in providing samples at any lower activity.

With regard to our future participation in a routine ORNL low-level intercomparison study we invite your input on the following issues:

1. That we would participate in low-level plutonium in urine intercomparison study on a quarterly basis. We envision that this low-level study would be offset from the current ORNL plutonium in urine intercomparison study.

2. That we would continue to participate in the current ORNL plutonium in urine study without change for assessment of both CST-9 and CST-11 alpha spectroscopy capabilities.

3. At current the plutonium spike standard used by ORNL doesn't have a know value for plutonium-240. Should we require the ORNL use a plutonium spike standard with a known plutonium-240 value?

4. With three samples in each study should we request that the activity of at least one sample be such that we could assess our plutonium-240 quantitation performance? If so, what activity level would be necessary? Or do we request samples with enhanced abundance of plutonium-240?

Distribution:

Dawn Lewis, ESH-12

Pat Brug, CST-3, MS K484
Peggy Gautier, CST-3, MS K484
Nancy Koski, CST-3, MS K484
Carolyn Macdonell, CST-3, MS K484
Jose Olivares, CST-9, MS K484
Edward Gonzales, CST-9, MS K484
Glenn Bentlley, CST-11, MS J514
Moses Attrep, CST-11, MS J514
Tim Benjamin, CST-11, MS J514
Donald Dry, CST-11, MS J514
Wes Efurd, CST-11, MS J514

Moses Attrep, 03:03 PM 8/6/97 +, Re: Intercomparison Results-LA

X-Sender: 098804@cstnt1.lanl.gov
Date: Wed, 6 Aug 1997 15:03:17 +0100
To: Ken Inn <kenneth.inn@nist.gov>
From: Moses Attrep <mattrep@lanl.gov>
Subject: Re: Intercomparison Results-LANL

Ken: Here is the value reported on the final revised report:

Sample 00.35880:
Total activity (Bq) in Each Bottle: 2.04 E-05 ✓
Massic Activity (Bq/g): 9.36 E-08 ✓
Uncertainty: 184.3% ✓

Hope this is what you need.

Moses

PS Did you get the forms for the visitor?

>Dr. Attrep:
>
>Could you please tell me, again, what value you got for #61,
00.35880? I've
>lost the value you gave me over the phone.
>
>Thanks,
>
>Ken
>
>PS: We got the visitor's forms. I used to have a "Q" clearance, but
the
>management here thought my job was low risk and removed my clearance.
>
>
>
>At 11:26 AM 6/5/97 +0100, you wrote:
>>Ken:
>>
>>Thanks for talking with us the other day. I have attached the final
>>results for the Yankee Atomic samples. As we indicated when talking
with
>>you the value of the one sample (#61, 00.35880) did change, but
checking
>>the calculations of the other one we found no change.
>>
>>I have also attached some comments with the results.
>>
>>Donivan has looked through ANSI 13.30 and did not find the synthetic
urine
>>recipe. We are still looking around. Meanwhile, I'd appreciate
getting

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>>what was used in this study and compare it with the recipe we used.
>>
>>Thanks.
>>
>>Moses
>>
>>Attachment Converted: C:\EUDORA\ENCL\Yankee_A.doc
>>Moses Attrep, Jr.
>>Los Alamos National Laboratory
>>MS J514
>>Los Alamos, NM 87545
>>505 667-0088
>>E-Mail: mattrep@lanl.gov
>>

Moses Attrep, Jr.
Los Alamos National Laboratory
MS J514
Los Alamos, NM 87545
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Attachment VIII

PNNL ICP-MS Report

Battelle
Pacific Northwest Laboratories

902 Battelle Blvd
P.O. Box 999
Richland, WA 99352

Fax Cover Sheet

DATE: 6/11/97

TO: Ken Inn
NIST

PHONE: 301 975 5541
FAX: 301 869 7682

FROM: Eric Wyse

PHONE: 376-3074
FAX: 376-7475

Number of pages including cover sheet:

Message

Ken - here's the data on the sheets as requested. Some of the errors may be over-estimated — we can discuss later. I'll type up our prep procedure + analysis + get that out to you later this afternoon. I figured you could use this information first.

Eric

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Results of Measurement
$^{239/240}$Pu in Artificial Urine

1. Please use this data reporting form for the submission of analytical results. Twenty-five samples of $^{239/240}$Pu spiked unstable artificial urine (> 10000 aCi/sample) have been provided for this study. Please analyze the total content of each bottle of sample, and report the individual measurement results. The reference date and time for your reported results is:

   12:00 noon EST, February 26, 1997

2. Report measurements in $Bq \cdot g^{-1}$ of solution. Report total combined standard uncertainty as 1s (%).

Sample Number	Total Activity (Bq) in each Bottle	Massic Activity ($Bq \cdot g^{-1}$)	Uncertainty (% 1s)
PuR0297-02	3.4×10^{-5}	1.7×10^{-7}	49%
03	6.7×10^{-5}	3.2×10^{-7}	49%
07	1×10^{-4}	5×10^{-7}	80% (est.)
10	$< 1 \times 10^{-5}$	$< 5 \times 10^{-8}$	
14	4.8×10^{-5}	2.3×10^{-7}	30%
17	2×10^{-5}	9×10^{-8}	70%
23	2.3×10^{-5}	1.1×10^{-7}	67%
24	2.1×10^{-5}	9.4×10^{-8}	40%
28	1.2×10^{-4}	5.5×10^{-7}	46%
30	$< 1 \times 10^{-5}$	$< 5 \times 10^{-8}$	
34	$< 2 \times 10^{-5}$	$< 1 \times 10^{-7}$	
38	$< 2 \times 10^{-5}$	$< 1 \times 10^{-7}$	
43	$< 2 \times 10^{-5}$	$< 1 \times 10^{-7}$	
49	7.1×10^{-5}	3.2×10^{-7}	30%
55	7×10^{-6}	3×10^{-8}	100%
56	1.1×10^{-4}	5.1×10^{-7}	27%

Kinn/doeehpu

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PuR0297 - 64	2.5×10^{-5}	1.2×10^{-7}	40%
67	3.7×10^{-5}	1.6×10^{-7}	50%
69	4.6×10^{-5}	2.0×10^{-7}	28%
72	2.8×10^{-5}	1.3×10^{-7}	112%
76	2.3×10^{-5}	1.0×10^{-7}	59%
88	7.3×10^{-5}	3.5×10^{-7}	30%
94	7.8×10^{-5}	3.6×10^{-7}	47%
97	1.1×10^{-4}	5.0×10^{-7}	35%
99	8.0×10^{-5}	3.9×10^{-7}	31%

3. State the ±1s "standard uncertainty" components (random and systematic) which comprise the combined standard uncertainty. These may include, but are not limited to the following:

Uncertainty due to calibration factor/efficiency = ~~0~~ %. (See tracer calib below)
1 Uncertainty due to dilutions/source preparation = ~~0~~ %.
Uncertainty due to impurity corrections = ~~0~~ %.
2 Uncertainty due to tracer calibration = 10 %.
Uncertainty due to gravimetric measurements = 1 %.
3 Uncertainty due to spectral interferences = 20 %.
4 Others; please describe.

1 Prep errors should be corrected by use of isotopic tracer
2 Tracer was not calibrated for this run. Previous calibrations have indicated very close correlation with our Pu-239 std on a mass basis. Error conservatively estimated at 10%.
3 Varied depending on concentration. Attributed exclusively to background/signal:noise ratio.
4 a. Precision between replicate runs; varied - averaged ~10%.
b. Blank - variability in $^{239}/_{245}$ ratio in blanks.

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6. Using actual measurement data, calibration factors, corrections, etc., give a sample calculation showing how the massic activity and uncertainty values reported in section 2 were determined. Identify all values used, e.g., efficiency, calibration factors, mass, volume, decay correction, etc.). **Attach a separate sheet if necessary**.

Sample 99

Integrated counts

m/z 238	239	244	245
673000.	278	63,138	89

Errors

a. Tracer calib est. 10%

b. Grav. measurement est. 1%

c. Bkg/spectral: $3 \cdot \sqrt{89} = 28$ cts (MDL)

Net 239 cts = 278 − 89 = 189 cts

$28/189 = 15\%$

d. Blank: $^{239}/_{245}$ ratios = 0.98, 0.967, 0.99, 1.22, 1.05, 1.43, 1.41, 1.41, 0.85 $\sigma = 23\%$

e. Precision: 34.5 (Run 2)
30 (Run 1)

Ave = 32 $\sigma = 3$ $\frac{\sigma}{\bar{x}} = 10\%$

$$\text{Total} = \sqrt{(10)^2 + (1)^2 + (15)^2 + (23)^2 + (10)^2} = 31\%$$

(Tracer, Gravimetric, BKG, BLK, Precision)

7. The deadline for submitted results is May 16, 1997. Please address results and technical questions to:

Kenneth G.W. Inn
NIST
245/C114
Gaithersburg, MD 20899

Phone: 301-975-5541
Fax: 301-869-7682
email: kenneth.inn@nist.gov

Kinn/doeehpu

Battelle
Pacific Northwest Laboratories

902 Battelle Blvd
P.O. Box 999
Richland, WA 99352

Fax Cover Sheet

DATE: 6/11/97

TO: Ken Inn
NIST

PHONE: 301 975 5541
FAX: 301 869 7682

FROM: Eric Wyse

PHONE: 376-3074
FAX: 376-7475

Number of pages including cover sheet:

Message

Ken - I noticed that the Results page indicates ^{239}Pu AND ^{240}Pu. I seem to remember noticing and inquiring about this earlier, but I forget what the answer was. The reported results are ONLY for Pu-239. We could have looked for 240, but unless there was a similar Mass of that isotope present, we probably wouldn't have been able to see it. Once again, the activities reported were converted directly from the mass obtained for Pu-239 - it DOES NOT account for activity due to Pu-240. Please call with any questions. Eric

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Results of Measurement ^{239}Pu in Artificial Urine: Questions 4 and 5

June 11, 1997

4) Sample preparation started on May 19. Each sample was transferred as quantitatively as possible to a tared 400 mL beaker and weighed. A 30 mL concentrated nitric acid aliquot was then added to the sample container; it was swirled around the walls for a few seconds, then transferred to the 400 mL sample beaker. To the acidified sample, 100µL of a 116 pg/mL ^{244}Pu solution was weighed and added as a tracer and internal standard. The acidified samples were digested by heating at 90°C for ~2 hours. The plutonium was then coprecipitated with calcium phosphate. The precipitate was isolated and redissolved and wet-ashed with nitric acid and hydrogen peroxide. After a clear solution was obtained, the residue was dissolved in ~3 mL 2M HNO_3. A microcolumn of TEVA-Spec™ resin was prepared by passing a resin/water slurry through a syringe filter. The microcolumn is first conditioned with 2 mL 2M HNO_3 before passing the dissolved residue. After passing the sample, the column is then rinsed with 2 mL 2M HNO_3, then reconditioned with 3 mL 6M HCl, and finally eluted with 2 mL deionized water into 10 mL plastic test tubes. All samples were eluted by May 27.

On May 29, the samples test tubes were placed in a hot water bath to reduce sample volume by evaporation. The target volume was 0.5 mL. By COB May 30, the volume had only been reduced down to just under 1 mL. The samples were removed from the heat and left uncovered over the weekend. By June 2 the volume had reduced to the target value of ~0.5 mL. Instrument sensitivity and background were both fairly good when the first sample analysis started on June 2. More than half of the samples were completed on June 2. The samples were covered with Parafilm overnight. Instrument sensitivity waned considerably after continuing the batch run on June 3. Samples were re-covered while instrument maintenance was performed to improve instrument response. Performance returned on

June 6. The second analysis was started Friday (6/6), but other instrument problems persisted on Friday and over the weekend. 'Kinks' were finally ironed out on Monday, June 9 (nebulizer cleared, good sensitivity, low background), and the analysis was completed by Monday evening.

5) Samples were analyzed on a VG Plasmaquad II+ using the 'S-option' enhanced-sensitivity interface. A membrane desolvation microconcentric nebulizer (MCN-6000 from Cetac) self-aspirating at ~20μL/min was used for sample introduction. A 10 minute data acquisition in peak-hopping mode (9 channels per peak) was made for each sample.

Calculations were done manually ('hand calculations') based on the peak integrals obtained for m/z 239 (isotope of interest), 244 (tracer), and 245 (designated background). The ^{239}Pu concentration was determined by comparing the net counts of m/z 239 with the counts obtained at m/z 244 for a known quantity of Pu. The 238 peak was also monitored to indicate excessive uranium concentrations. The uncertainty values were calculated as described on the Results report (question 6). An Excel 5.0 spreadsheet was used to facilitate all calculations.

IV.

MEASUREMENT RESULTS and DATA ANALYSIS

Mean, Standard Deviation and Bias

The deviations from the NIST values for each determination, the average deviation from the NIST values, and the standard deviation were determined for the data that survived the outlier tests. Spreadsheets 1, 2, 3 and 4 report the measurement results for the participating laboratories. Table 4 summarizes the determination of the Total Propagated Uncertainties (K=1).

The spreadsheets list the following information:

ID	Sample Identification Number
Avg/1s	Mean value and 1 standard deviation of the reported values
Target	Target solution concentration in aCi/sample
Sample Mass	Mass of sample solution
Known	NIST ^{239}Pu concentration value of the sample solution as nBq/g and nBq/sample
Sigma1%	1 sigma total propagated uncertainty of the NIST value in percent
Measured	Reported ^{239}Pu per sample as nBq/sample and percent sigma total propagated uncertainty
Bias%	Percent difference between the NIST and reported nBq/sample value
Notes	Reason for not including the measured value in the assessment
Measured	Reported ^{239}Pu per sample as nBq/g and percent sigma total propagated uncertainty
Bias%	Percent difference between the NIST and reported nBq/g value

Spreadsheets 1-4

Measurement Results and Data Analysis

C	A	B	C	D	E	F	G	H	I	J	K	L	M
1	BNL-ICPMS												
2													
3		Target	SampleMass	Known			Measured		Bias%	Notes	Measured		Bias%
4	ID	aCi/Sample	g	nBq/g	nBq/Sample	Sigma1%	nBq/Sample	Sigma1%			nBq/g	Sigma1%	
5	18	BLK	207	0	0		100	250			0.3		
6	46	BLK	204.45	0	0		*-3800			Low CY	*-19		
7	71	BLK	201.5	0	0		-800	31.3			-4.1		
8	92	BLK	195.65	0	0		600	41.7			3		
9	100	BLK	228.85	0	0		200	75			0.7		
10	Avg/1sm						25	1181.807			-0.025	-5931.55	
11	sm(nBq/unit)							295.4516				1.482889	
12	16	100	215.7	18.5114	3992.90898	0.5	3400	7.3	-14.85		16	7.3	-13.57
13	36	100	224.2	18.5114	4150.25588	0.5	*9600			Outlier?	*43		
14	58	100	220.4	18.5114	4079.91256	0.5	3300	7.6	-19.12		15	7.6	-18.97
15	65	100	222.5	18.5114	4118.7865	0.5	2800	7.1	-32.02		12	7.1	-35.18
16	75	100	222.2	18.5114	4113.23308	0.5	3600	6.9	-12.48		16	6.9	-13.57
17	Avg/1sm					0.5	3275	5.196076	-19.62		14.75	6.416846	-20.32
18													
19	26	250	221.65	46.2934	10260.9321	0.5	9000	2.8	-12.29		40	2.8	-13.59
20	29	250	205.35	46.2934	9506.34969	0.5	7700	2.6	-19		38	2.6	-17.91
21	32	250	217.6	46.2934	10073.4438	0.5	8500	5.6	-15.62		39	5.6	-15.75
22	54	250	212.9	46.2934	9855.86486	0.5	8800	2.8	-10.71		41.5	2.8	-10.35
23	85	250	215.1	46.2934	9957.71034	0.5	9400	2.7	-5.601		44	2.7	-4.954
24	Avg/1sm					0.5	8680	3.286945	-12.64		40.5	2.589651	-12.51
25													
26	44	800	208.25	148.368	30897.636	0.5	28400	0.9	-8.084		136	0.9	-8.336
27	52	800	210.75	148.368	31268.556	0.5	*31300			Outlier?	*149		
28	74	800	210.7	148.368	31261.1376	0.5	28300	0.9	-9.472		134	0.9	-9.684
29	81	800	214.8	148.368	31869.4464	0.5	29200	0.7	-8.376		136	0.7	-8.336
30	87	800	215.5	148.368	31973.304	0.5	29700	0.8	-7.11		138	0.8	-6.988
31	Avg/1sm					0.5	28900	1.156282	-8.261		136	0.600365	-8.336
32													
33	35	1500	213.45	277.747	59285.0972	0.5	54900	0.5	-7.397		257	0.5	-7.47
34	57	1500	211.25	277.747	58674.0538	0.5	55600	0.4	-5.239		263	0.4	-5.31
35	70	1500	228.15	277.747	63367.9781	0.5	58100	0.4	-8.313		255	0.4	-8.19
36	79	1500	217.1	277.747	60298.8737	0.5	55900	0.4	-7.295		257	0.4	-7.47
37	84	1500	221.3	277.747	61465.4111	0.5	57900	0.3	-5.801		262	0.3	-5.67
38	Avg/1sm					0.5	56480	1.137011	-6.809		258.8	0.603574	-6.822

28

C	S	T	U	V	W	X	Y	Z	AA
3	NOSM	Meas						AccCrit	Pass/Fail
4		nBq/g							
5		-19	Regression Output:						
6	-1	-4.1	Constant			-0.025			
7	-0.29	0.3	Std Err of Y Est			1.08901			
8	0.29	0.7	R Squared			0.910113	0.953999	>0.868	Pass
9	1	3	No. of Observations			4			
10			Degrees of Freedom			2			
11	x,stds,del[9]	-0.025	2.965777	ERR					
12			X Coefficient(s)		3.328106				
13			Std Err of Coef.		0.739575				
14									
15	-1	12	Regression Output:						
16	-0.29	15	Constant			14.75			
17	0.29	16	Std Err of Y Est			1.063439			
18	1	16	R Squared			0.789599	0.888594	>0.868	Pass?
19		43	No. of Observations			4			
20			Degrees of Freedom			2			
21	x,stds	14.75	1.892969	-20.3194					
22			X Coefficient(s)		1.9786				
23			Std Err of Coef.		0.722209				
24									
25	-1.13	38	Regression Output:						
26	-0.49	39	Constant			-14.7365			
27	0	40	Std Err of Y Est			0.201057			
28	0.49	41.5	R Squared			0.960029	0.979811	>0.879	Pass
29	1.13	44	No. of Observations			5			
30			Degrees of Freedom			3			
31	x,stds	40.5	2.345208	-12.5145					
32			X Coefficient(s)		0.363864				
33			Std Err of Coef.		0.042865				
34									
35	-1	134	Regression Output:						
36	-0.29	136	Constant			136			
37	0.29	136	Std Err of Y Est			0.557049			
38	1	138	R Squared			0.922424	0.960429	>0.868	Pass
39		149	No. of Observations			4			
40			Degrees of Freedom			2			
41	x,stds	138.6	5.98331	-6.58363					
42			X Coefficient(s)		1.844848				
43			Std Err of Coef.		0.378306				
44									
45	-1.13	255	Regression Output:						
46	-0.49	257	Constant			-60.9347			
47	0	257	Std Err of Y Est			0.330993			
48	0.49	262	R Squared			0.891671	0.944283	>0.879	Pass
49	1.13	263	No. of Observations			5			
50			Degrees of Freedom			3			
51	x,stds	258.8	3.49285	-6.82168					
52			X Coefficient(s)		0.235451				
53			Std Err of Coef.		0.047382				

B	A	B	C	D	E	F	G	H	I	J	K	L	M
1	BNL-FTA												
2													
3		Target	SampleMass	Known			Measured		Bias%	Notes	Measured		Bias%
4	ID	aCi/Sample	g	nBq/g	nBq/Sam	Sigma1%	nBq/Sample	Sigma1%			nBq/g	Sigma1%	
5	6	BLK	225	0	0		700	42.9			3		
6	8	BLK	216.5	0	0		1700	17.6			8		
7	62	BLK	203.7	0	0		LOST			Lost	Lost		
8	83	BLK	199.6	0	0		*<700			<LLD	<3.5		
9	96	BLK	231.4	0	0		*<700			<LLD	<3.0		
10	Avg/1sm						1200	57.83517			5.5	59.38157	
11	sm(nBq/unit)							500				2.5	
12	1	100	219	18.5114	4053.997	0.5	*<700			<LLD	<3.2		
13	4	100	225.6	18.5114	4176.172	0.5	2500	12	-40.14		11	12	-40.58
14	41	100	234	18.5114	4331.668	0.5	18200	1.9	320.2	mislabled?	78	1.9	321.4
15	60	100	215.9	18.5114	3996.611	0.5	3100	9.7	-22.43		14	9.7	-24.37
16	63	100	227.6	18.5114	4213.195	0.5	2900	12.1	-31.17		13	12.1	-29.77
17	Avg/1sm					0.5	2833.33333	5.391266	-31.25		12.66667	6.029705	-31.57
18													
19	31	250	217.66	46.2934	10076.22	0.5	11400	2.6	13.14		52	2.6	12.33
20	40	250	221.7	46.2934	10263.25	0.5	10000	3.5	-2.565		45	3.5	-2.794
21	53	250	221.35	46.2934	10247.04	0.5	6900	4.3	-32.66		31	4.3	-33.04
22	59	250	227.35	46.2934	10524.8	0.5	6100	4.9	-42.04		27	4.9	-41.68
23	91	250	223.95	46.2934	10367.41	0.5	3200	14.1	-69.13		14	14.1	-69.76
24	Avg/1sm					0.5	7520	19.33183	-26.65		33.8	19.87761	-26.99
25													
26	15	800	220.5	148.368	32715.14	0.5	*<700			<LLD	<3.2		
27	20	800	209.4	148.368	31068.26	0.5	23200	1.5	-25.33		100	1.5	-32.6
28	50	800	212.8	148.368	31572.71	0.5	2600	11.5	-91.77	mislabled?	12	11.5	-91.91
29	51	800	213.9	148.368	31735.92	0.5	9100	3.3	-71.33		42	3.3	-71.69
30	80	800	211.85	148.368	31431.76	0.5	34100	1.2	8.489		161	1.2	8.514
31	Avg/1sm					0.5	22133.3333	28.31496	-29.39		101	29.45857	-31.93
32													
33	12	1500	220.2	277.747	61159.89	0.5	27100	1.3	-55.69		123	1.3	-55.72
34	33	1500	206.1	277.747	57243.66	0.5	LOST			Lost	Lost		
35	42	1500	207.1	277.747	57521.4	0.5	57000	0.9	-0.906		275	0.9	-0.989
36	73	1500	206.7	277.747	57410.3	0.5	48900	0.9	-14.82		237	0.9	-14.67
37	93	1500	207.7	277.747	57688.05	0.5	*21600	6.2		trackoverlap	*104		
38	Avg/1s					0.5	44333.3333	20.13901	-23.81		211.6667	21.57653	-23.79

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B	S	T	U	V	W	X	Y	Z	AA
3	NOSM	Meas							
4		nBq/g							
5		3							
6		8							
7		lost							
8		<5.5							
9		<5.5							
10	x,stds,del9	5.5	64.28243						
11									
12									
13									
14									
15		<5.5	Regression Output:						
16	-0.82	11	Constant			12.66667			
17	0	13	Std Err of Y Est			0.408248			
18	0.82	14	R Squared			0.964286	0.981981	>0.879	Pass
19		78	No. of Observations			3			
20			Degrees of Freedom			1			
21	x,stds	12.66667	1.527525	-31.5737					
22			X Coefficient(s)		1.829268				
23			Std Err of Coef.		0.352043				
24									
25	-1.13	14	Regression Output:						
26	-0.49	27	Constant			33.8			
27	0	31	Std Err of Y Est			2.567429			
28	0.49	45	R Squared			0.978096	0.988987	>0.879	Pass
29	1.13	52	No. of Observations			5			
30			Degrees of Freedom			3			
31	x,stds	33.8	15.02332	-26.9874					
32			X Coefficient(s)		-17.06				
33			Std Err of Coef.		1.473977				
34									
35		<3.2	Regression Output:						
36		12	Constant			101			
37	-0.82	42	Std Err of Y Est			1.224745			
38	0	100	R Squared			0.999788	0.999894	>0.879	Pass
39	0.82	161	No. of Observations			3			
40			Degrees of Freedom			1			
41	x,stds	101							
42			X Coefficient(s)		72.56098				
43			Std Err of Coef.		1.056129				
44									
45		104	Regression Output:						
46	-0.82	123	Constant			211.6667			
47	0	237	Std Err of Y Est			31.02687			
48	0.82	275	R Squared			0.923077	0.960769	>0.879	Pass
49		lost	No. of Observations			3			
50			Degrees of Freedom			1			
51	x,stds	211.6667							
52			X Coefficient(s)		92.68293				
53			Std Err of Coef.		26.75526				

A	A	B	C	D	E	F	G	H	I	J	K	L	M
1	LANL												
2													
3		Target	SampleMass	Known			Measured		Bias%	Notes	Measured		Bias%
4	ID	aCi/Sample	g	nBq/g	nBq/Sample	Sigma1%	nBq/Sample	Sigma1%			nBq/g	Sigma1%	
5	68	BLK	201	0	0		<-1780	249.1		<LLD	<-8.84	249.1	
6	77	BLK	195.4	0	0		28300	31.6			145	31.6	
7	86	BLK	208.8	0	0		-2310	195.4			-11.1	195.4	
8	90	BLK	205.95	0	0		11500	39			56	39	
9	98	BLK	209	0	0		-1490	294.4			-7.14	294.4	
10	Avg/1sm						9000	79.65307			45.69	79.88091	
11	sm(nBq/unit)							7168.776				36.49759	
12	37	100	219.7	18.5114	4066.95458	0.5	6450	70.2	58.6		29.3	70.2	58.28
13	45	100	222.3	18.5114	4115.08422	0.5	8830	58.4	114.6		39.7	58.4	114.5
14	48	100	216.1	18.5114	4000.31354	0.5	6900	66.7	72.49		31.9	66.7	72.33
15	66	100	218.4	18.5114	4042.88976	0.5	7830	59.5	93.67		35.9	59.5	93.93
16	82	100	223.8	18.5114	4142.85132	0.5	6990	78.2	68.72		31.3	78.2	69.08
17	Avg/1sm					0.5	7400	5.693665	81.61		33.62	5.531462	81.62
18													
19	25	250	224.7	46.2934	10402.127	0.5	19000	35.5	82.65		84.4	35.5	82.32
20	39	250	218.4	46.2934	10110.4786	0.5	15500	32.9	53.31		71.2	32.9	53.8
21	47	250	222.1	46.2934	10281.7641	0.5	17600	28.5	71.18		79.4	28.5	71.51
22	78	250	203.95	46.2934	9441.53893	0.5	<16800			<LLD	<82.6		
23	89	250	217.6	46.2934	10073.4438	0.5	12800	37.2	27.07		59	37.2	27.45
24	Avg/1sm					0.5	16225	8.316212	58.55		73.5	7.546218	58.77
25													
26	9	800	214.1	148.368	31765.5888	0.5	47700	12.2	50.16		223	12.2	50.3
27	11	800	216.75	148.368	32158.764	0.5	27800	17.6	-13.55		128	17.6	-13.73
28	13	800	211.3	148.368	31350.1584	0.5	23100	19.4	-26.32		109	19.4	-26.53
29	19	800	205.85	148.368	30541.5528	0.5	36200	17.1	18.53		176	17.1	18.62
30	22	800	220.1	148.368	32655.7968	0.5	22300	22.5	-31.71		101	22.5	-31.93
31	Avg/1sm					0.5	31420	15.15353	-0.578		147.4	15.57221	-0.652
32													
33	5	1500	224.1	277.747	62243.1027	0.5	74000	8.2	18.89		330	8.2	18.81
34	21	1500	216.4	277.747	60104.4508	0.5	<74500			<LLD	<344		
35	27	1500	214.1	277.747	59465.6327	0.5	54400	8.7	-8.519		254	8.7	-8.55
36	61	1500	218.1	277.747	60576.6207	0.5	20400	184.3	-66.32		93.6	184.3	-66.3
37	95	1500	221.7	277.747	61576.5099	0.5	109000	13.9	77.02		492	13.9	77.14
38	Avg/1sm					0.5	64450	28.74043	5.265		292.4	28.3139	5.276

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A	S	T	U	V	W	X	Y	Z	AA
3	NOSM	Meas							
4		nBq/g							
5		<-8.84		Regression Output:					
6	-1	-11.1	Constant			45.69			
7	-0.29	-7.14	Std Err of Y Est			31.26699			
8	0.29	56	R Squared			0.877681	0.936847	>0.868	Pass
9	1	145	No. of Observations			4			
10			Degrees of Freedom			2			
11	x,stds	45.69							
12			X Coefficient(s)		80.44027				
13			Std Err of Coef.		21.23422				
14									
15	-1.13	29.3		Regression Output:					
16	-0.49	31.3	Constant			33.62			
17	0	31.9	Std Err of Y Est			1.226299			
18	0.49	35.9	R Squared			0.934776	0.966838	>0.879	Pass
19	1.13	39.7	No. of Observations			5			
20			Degrees of Freedom			3			
21	x,stds	33.62	4.158365	81.61781					
22			X Coefficient(s)		4.616348				
23			Std Err of Coef.		0.704026				
24									
25		<82.6		Regression Output:					
26	-1	59	Constant			73.5			
27	-0.29	71.2	Std Err of Y Est			2.576897			
28	0.29	79.4	R Squared			0.964024	0.981847	>0.868	Pass
29	1	84.4	No. of Observations			4			
30			Degrees of Freedom			2			
31	x,stds	73.5							
32			X Coefficient(s)		12.81155				
33			Std Err of Coef.		1.750038				
34									
35	-1.13	101		Regression Output:					
36	-0.49	109	Constant			147.4			
37	0	128	Std Err of Y Est			17.64786			
38	0.49	176	R Squared			0.911329	0.954636	>0.879	Pass
39	1.13	223	No. of Observations			5			
40			Degrees of Freedom			3			
41	x,stds	147.4	51.32543	-0.65243					
42			X Coefficient(s)		56.25906				
43			Std Err of Coef.		10.13174				
44									
45		<344							
46	-1	93.6		Regression Output:					
47	-0.29	254	Constant			292.4			
48	0.29	330	Std Err of Y Est			18.99419			
49	1	492	R Squared			0.991227	0.995604	>0.868	Pass
50			No. of Observations			4			
51	x,stds	233.92	Degrees of Freedom			2			
52									
53			X Coefficient(s)		193.912				
54			Std Err of Coef.		12.89945				

D	A	B	C	D	E	F	G	H	I	J	K	L	M
1	PNNL												
2													
3				Known			Measured		Bias%	Notes	Measured		Bias%
4	ID	aCi/Sample	g	nBq/g	nBq/Sample	Sigma1%	nBq/Sample	Sigma1%			nBq/g	Sigma1%	
5	2	BLK	205.4	0	0		34000	49			170	49	
6	7	BLK	225.5	0	0		*100000	80		Low CY	*500	80	
7	10	BLK	206.1	0	0		<10000			<LLD	<50		
8	38	BLK	212.45	0	0		<20000			<LLD	<100		
9	76	BLK	221.85	0	0		23000	59			100	59	
10	Avg/1sm						28500	19.29825			135	25.92593	
11	sm(nBq/unit)							8131.728				35.35534	
12	24	100	219.8	18.5114	4068.80572	0.5	21000	40	416.1		94	40	407.8
13	43	100	223.5	18.5114	4137.2979	0.5	<20000			<LLD	<100		
14	55	100	234.6	18.5114	4342.77444	0.5	*7100	100		Low CY	*30	100	
15	67	100	228.95	18.5114	4238.18503	0.5	37000	50	773		160	50	764.3
16	69	100	230.3	18.5114	4263.17542	0.5	46000	28	979		200	28	980.4
17	Avg/1sm					0.5	34666.6667	21.08818	722.7		151.3333	20.42172	717.5
18													
19	17	250	214.7	46.2934	9939.19298	0.5	*20000	70		Low CY	*90	70	
20	30	250	213.2	46.2934	9869.75288	0.5	<10000			<LLD	<50		
21	34	250	213.5	46.2934	9883.6409	0.5	<20000			<LLD	<100		
22	49	250	223.5	46.2934	10346.5749	0.5	71000	30	586.2		320	30	591.2
23	64	250	220.1	46.2934	10189.1773	0.5	25000	40	145.4		120	40	159.2
24	Avg/1sm					0.5	48000	47.91667	365.8		220	45.45455	375.2
25													
26	14	800	214.65	148.368	31847.1912	0.5	48000	30	50.72		230	30	55.02
27	23	800	216.25	148.368	32084.58	0.5	23000	67	-28.31		110	67	-25.86
28	28	800	212.3	148.368	31498.5264	0.5	120000	46	281		550	46	270.7
29	72	800	213.9	148.368	31735.9152	0.5	28000	112	-11.77		130	112	-12.38
30	94	800	216.5	148.368	32121.672	0.5	78000	47	142.8		360	47	142.6
31	Avg/1sm					0.5	59400	30.25436	86.89		276	29.55953	86.02
32													
33	3	1500	208.5	277.747	57910.2495	0.5	67000	49	15.7		320	49	15.21
34	56	1500	209	277.747	58049.123	0.5	110000	27	89.49		510	27	83.62
35	88	1500	213.2	277.747	59215.6604	0.5	73000	30	23.28		350	30	26.01
36	97	1500	212.75	277.747	59090.6743	0.5	110000	35	86.15		500	35	80.02
37	99	1500	207.9	277.747	57743.6013	0.5	80000	31	38.54		390	31	40.42
38	Avg/1sm					0.5	88000	10.47059	50.63		414	9.373724	49.06

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D	S	T	U	V	W	X	Y	Z	AA
3	NOSM	Meas							
4		nBq/g							
5		170							
6		*500							
7		<50							
8		<100							
9		100							
10	x,stds	135	36.6648						
11									
12									
13									
14									
15		*30		Regression Output:					
16		<100	Constant			151.3333			
17	-0.82	94	Std Err of	Regression Output:		10.61446			
18	0	160	R Squared			0.98034	0.990121	>0.879	Pass
19	0.82	200	No. of Observations			3			
20			Degrees of Freedom			1			
21	x,stds	151.3333	35.37146						
22			X Coefficient(s)		64.63415	1			
23			Std Err of Coef.		9.153114				
24									
25		*90							
26		<50							
27		<100							
28		320							
29		120							
30									
31	x,stds	220	64.28243						
32									
33									
34									
35	-1.13	110		Regression Output:					
36	-0.49	130	Constant			276			
37	0	230	Std Err of Y Est			59.2082			
38	0.49	360	R Squared			0.920997	0.959686	>0.879	Pass
39	1.13	550	No. of Observations			5			
40			Degrees of Freedom			3			
41	x,stds	276	66.09713						
42			X Coefficient(s)		201.0218				
43			Std Err of Coef.		33.99179				
44									
45	-1.13	320		Regression Output:					
46	-0.49	350	Constant			414			
47	0	390	Std Err of Y Est			30.24263			
48	0.49	500	R Squared			0.908903	0.953364	>0.879	Pass
49	1.13	510	No. of Observations			5			
50			Degrees of Freedom			3			
51	x,stds	414	20.96028						
52			X Coefficient(s)		94.99011				
53			Std Err of Coef.		17.36248				

I	A	B	C	D	E	F	G	H	I
1	mda								
2									
3	lab	NIST	Reported	Random	Systemmatic	Random	Systemmatic	mda	mda
4		nBq/g	nBq/g	sm1%	sigma1%	sm1(nBq/g)	sigma1(nBq/g	nBq/g	at "0" nBq/g
5									
6	BNL ICP-MS	BLANK	-0.025	5931.55	10.7	1.4828875	0.002675	9.242649	7.9
7		18.5	14.8	6.416846	10.7	0.9496932	1.5836	6.993474	CL95% = 22%
8		46.3	40.5	2.589651	10.7	1.0488087	4.3335	7.40138	
9		148.4	136	0.600365	10.7	0.8164964	14.552	6.452636	
10		277.7	259	0.603574	10.7	1.5632567	27.713	9.593352	
11									
12	BNL FTA	BLANK	5.5	59.38157	18.9	3.2659864	1.0395	21.13697	6
13		18.5	12.7	6.029705	18.9	0.7657725	2.4003	6.826113	CL95% = 1900%
14		46.3	33.8	19.87761	18.9	6.7186322	6.3882	50.13683	
15		148.4	101	29.45857	18.9	29.753156	19.089	517.8243	
16		277.7	212	21.57653	18.9	45.742244	40.068	1122.893	
17									
18	LANL TIMS	BLANK	45.7	79.88091	0.287	36.505576	0.131159	131.1281	3
19		18.5	33.6	5.531462	0.287	1.8585712	0.096432	9.160743	CL95% = 585%
20		46.3	73.5	7.546218	0.287	5.5464702	0.210945	21.48596	
21		148.4	147	15.57221	0.287	22.891149	0.42189	81.55305	
22		277.7	292	28.3139	0.287	82.676588	0.83804	315.1431	
23									
24	PNNL ICP-M	BLANK	135	25.92593	22.4	35.000006	30.24	816.347	455
25		18.5	151	20.42172	22.4	30.836797	33.824	649.2829	CL95% = 3600%
26		46.3	220	45.45455	22.4	100.00001	49.28	5889.889	
27		148.4	276	29.55953	22.4	81.584303	61.824	3982.039	
28		277.7	414	9.373724	22.4	38.807217	92.736	985.7653	

Table 4

Uncertainty	BNL ICP-MS	BNL FTA	LANL TIMS	PNNL ICP-MS
Replicate & Random	($1s_m$, %)	($1s_m$, %)	($1s_m$, %)	($1s_m$, %)
Concentration (nBq/g)				
Blank	5900	59	80	26
18.5	6.4	6.0	5.5	20
46.3	2.6	20	7.5	45
148.4	0.60	29	16	30
277.7	0.60	22	28	9.4
Tracer	5.8	5.8	0.25	10
Chemical Yield	9	15	-	-
Other	-	10 (Thermal Flux)	0.1 (Geometry) 0.1 (Spectral Interference)	1 (Geometry) 20 (Spectral Interference)
Total Propagated Uncertainty				
Concentration (nBq/g)				
Blank	5900	62	80	34
18.5	12	20	5.5	30
46.3	11	27	7.6	51
148.4	11	35	16	37
277.7	11	29	28	24

Outlier Tests

Because the primary objective of this intercomparison is to evaluate the mass spectrometric technology for its ability to measure plutonium (239) in synthetic urine, the best reported data was to be used for the evaluation. Each laboratory was asked to review their data carefully for accuracy, and to note data that of poor confidence. Those data that were noted as unreliable were reported but not used in this evaluation. The remaining data were evaluated for normal distribution. Filliben's r criteria for goodness of fit of normal probability plots was used to detect outlying data (J.J. Filliben, The Probability Plot Correlation Coefficient Test for Normality, Technometrics, 17 (1), 111-117 (1975)). Outlier data were also not used in this evaluation. Included with the spreadsheets (1-4) are the assessment of the distribution of the reported nBq/g values. Normal probability plots of the data are displayed in Figures 1-17. The linearity of the data, r, is evaluated against the Filliben acceptance criteria. The spreadsheets include the following information:

NOSM	Normal Ordered Statistic Medians for each reported concentration value
Meas (nBq/g)	Reported concentration value
x, stds	Mean and percent standard deviation of reported concentration values
Regression Output	R squared is the goodness of the regression fit, followed by R, Filliben's acceptance criteria, and decision that the data is not statistically different from a normal distribution when R > Filliben's criteria

Technical Issues

The results of this study can now be used to address the technical issues raised during the design of the study protocol.

- Stability of the plutonium in glass bottles and in the synthetic urine: As a minimum, over the short-term of a few weeks and by washing the bottle with strong acid, the plutonium appears to be stable in the glass bottles and in the synthetic urine. BNL ICP-MS results indicate stability of the test samples to better than 8 percent at the 148-278 nBq/g levels, and better than 20 percent at the 15-41 nBq/g levels.

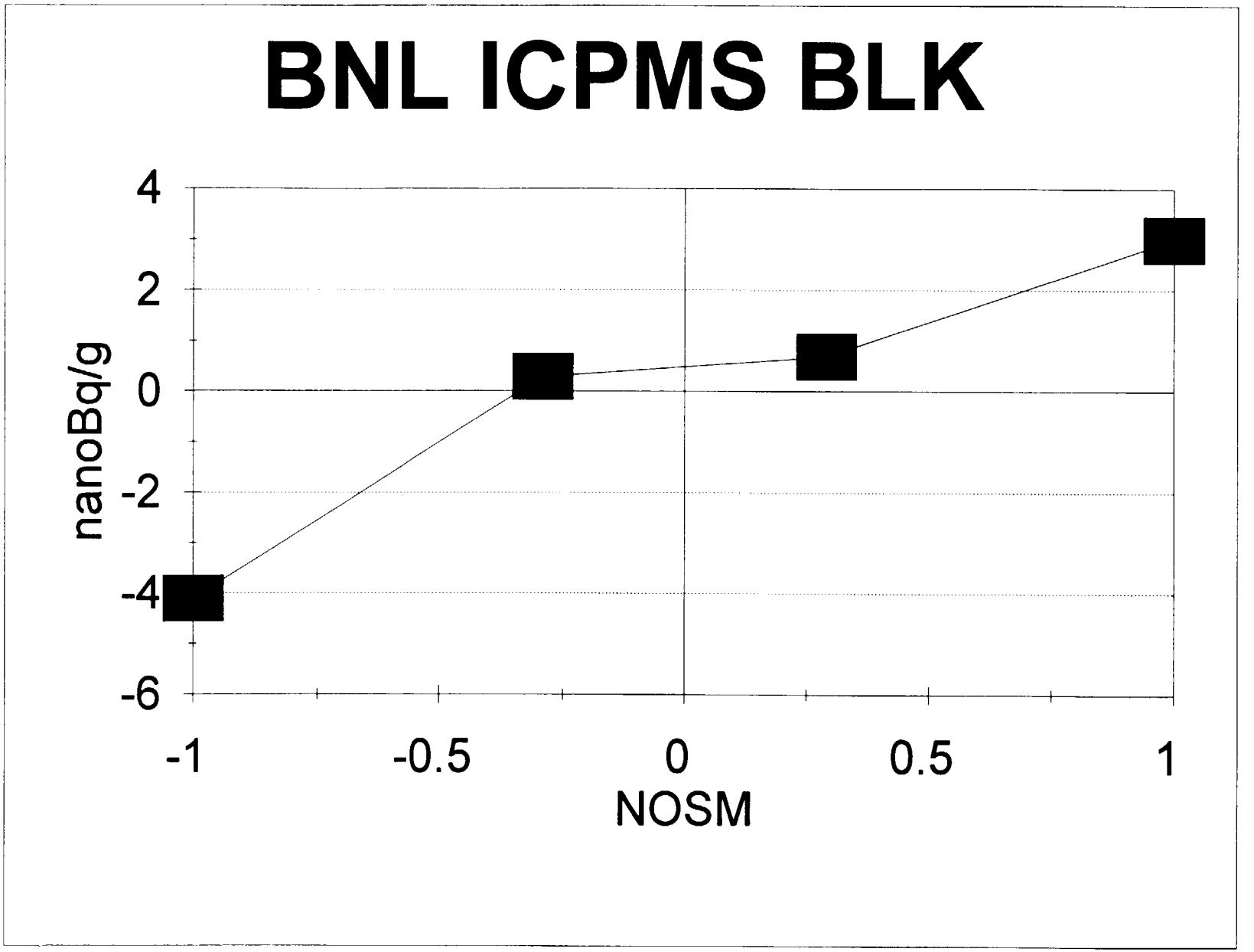
- Contamination from plutonium in the reagents used to make the synthetic urine: The BNL ICP-MS and FTA results indicate contamination of the test samples by plutonium in chemical reagents to be negligible (< 6 nB/g, and probably as low as ≈ 0.03 nBq/g).

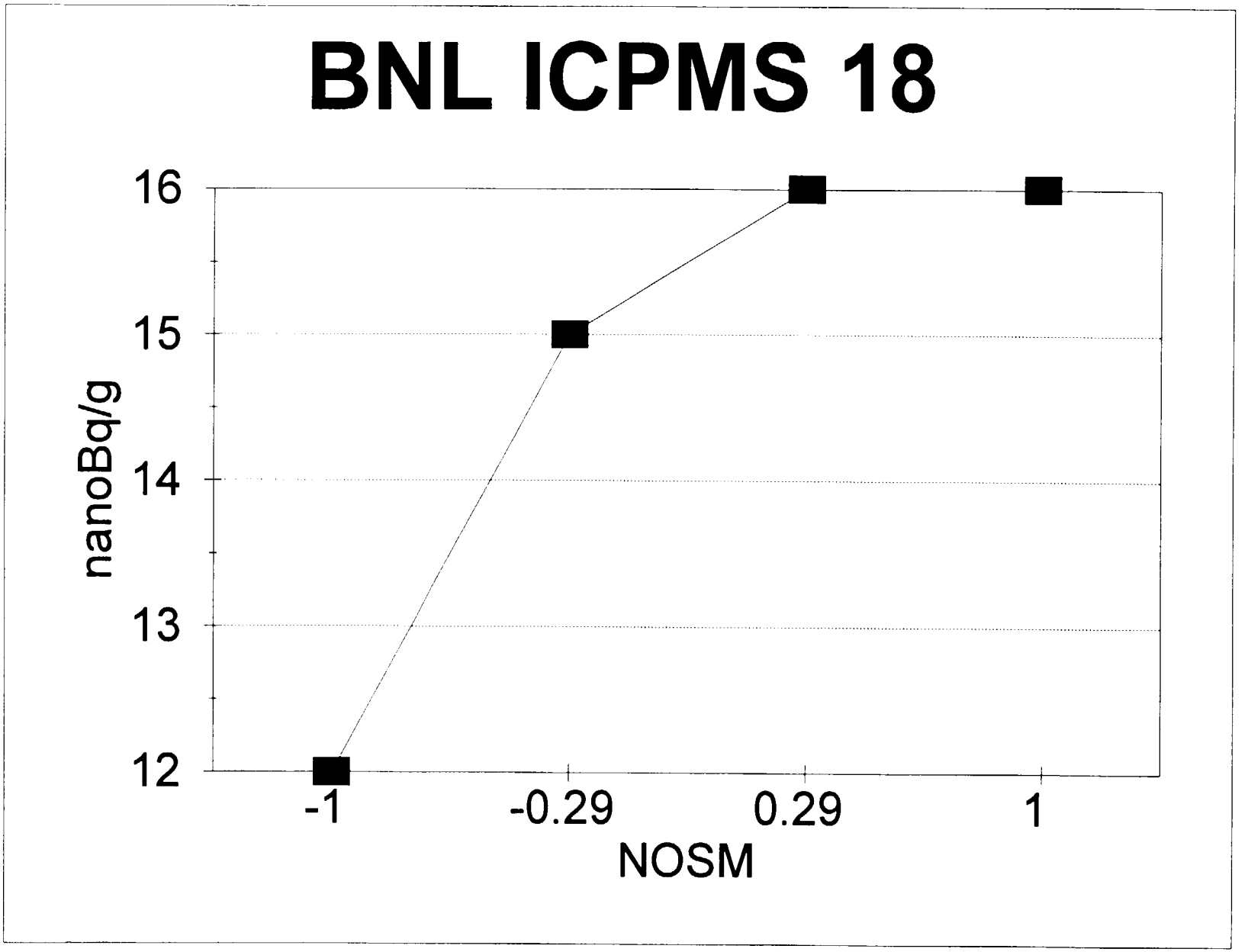
- Adequacy of the synthetic urine as a substitute for natural urine: The ANSI N13.30 standard allows use of synthetic urine as a test matrix, synthetic urine was used for pilot testing the efficacy of the ANSI N13.30 standard, and synthetic urine will be used for the radiobioassay DOE Laboratory Accreditation Program. However, it was pointed out by all of the participating laboratories that chemical yields were substantially lower than anticipated. For example, LANL reported chemical yields as low as 20 percent - their average chemical yield for radiourine assay is 80 percent. The low chemical yield substantially lowers analytical sensitivity and increases measurement uncertainty. A systematic study will be necessary at each laboratory to optimize chemical yield from synthetic urine analysis. It is likely, however, that the resulting analytical protocol will be substantially different from that in daily use for natural urine. None the less, the results of this study provides a lower limit to mass spectrometry's capabilities, from which improvements can be built.

Figures 1-5

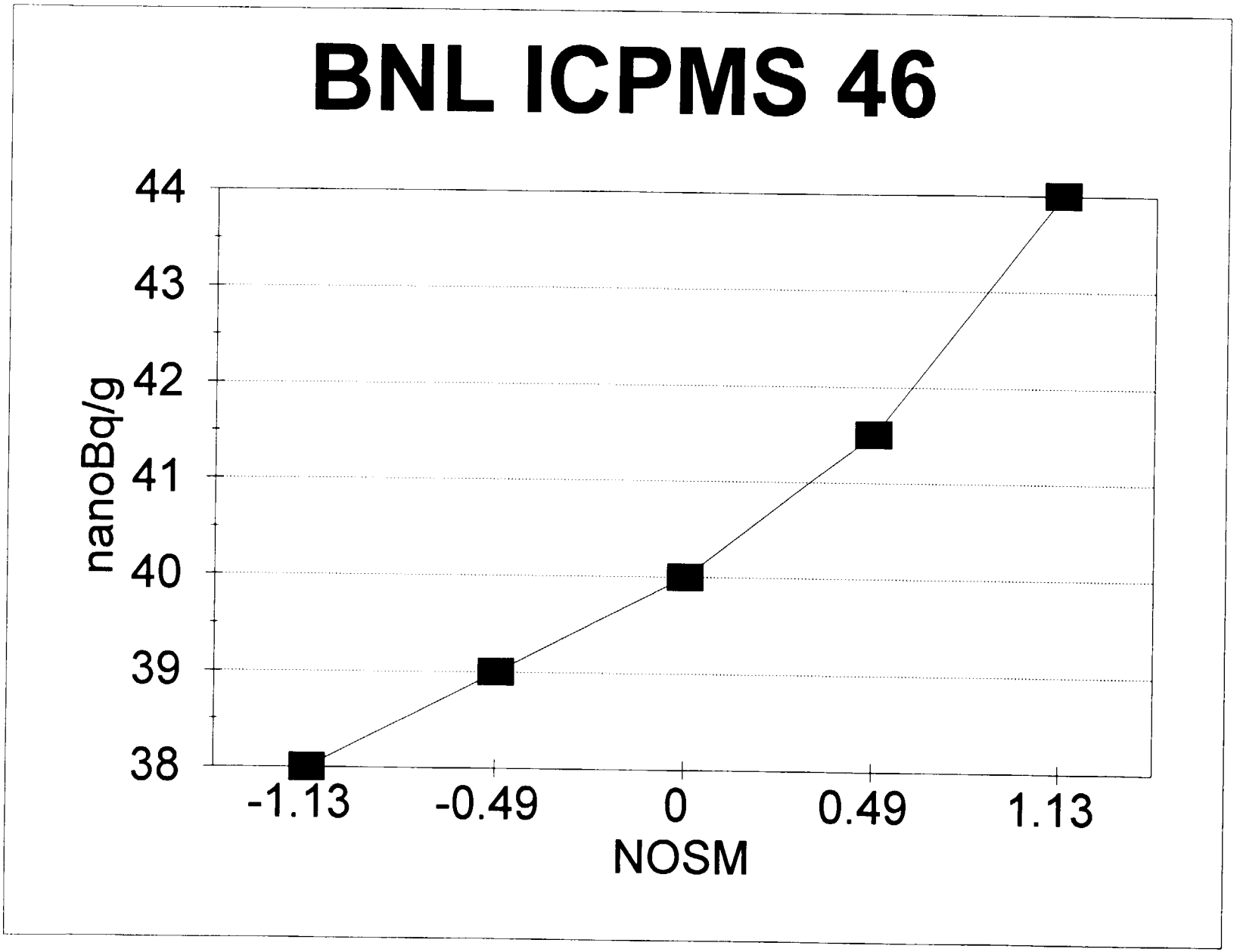
BNL ICP-MS

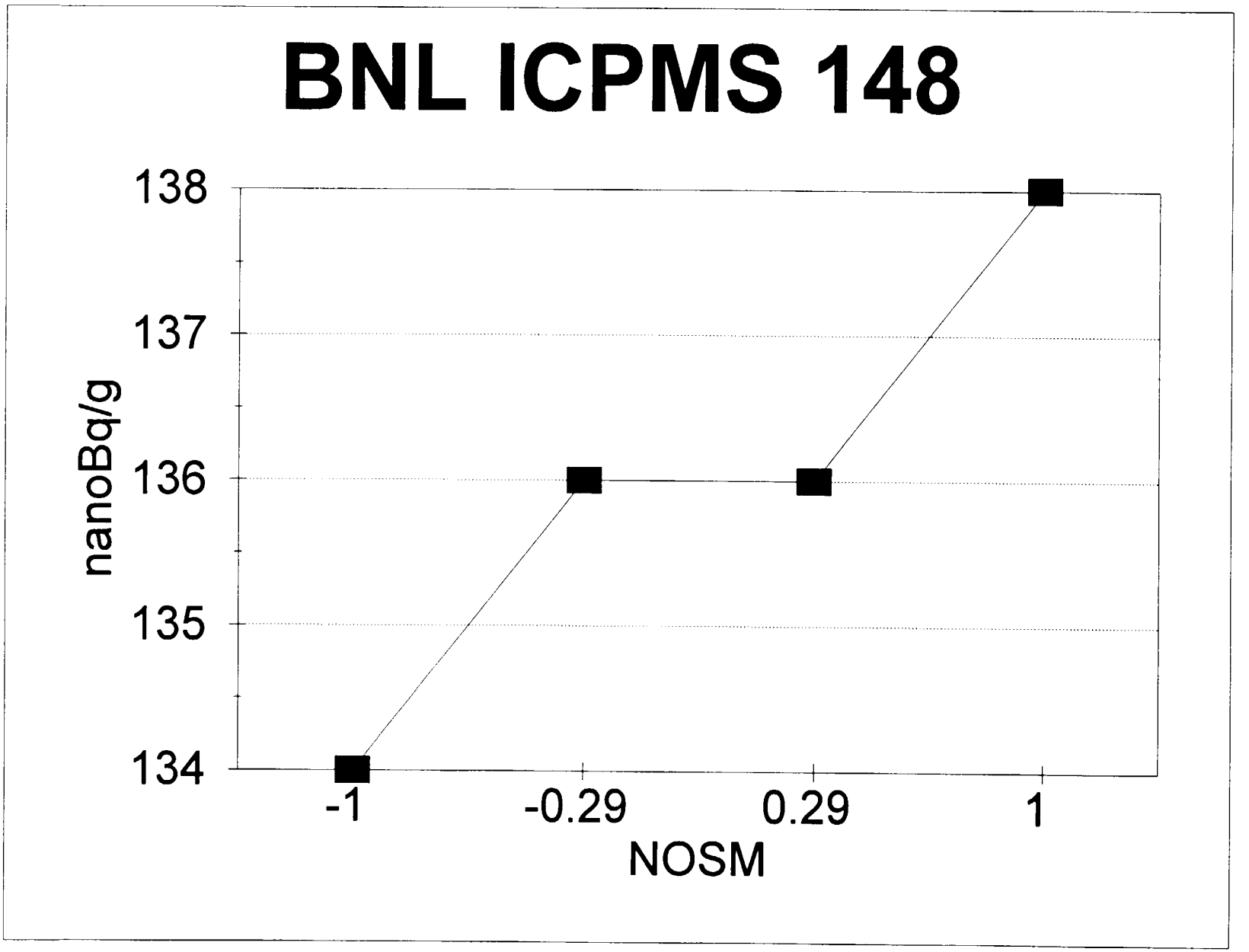
NOSM

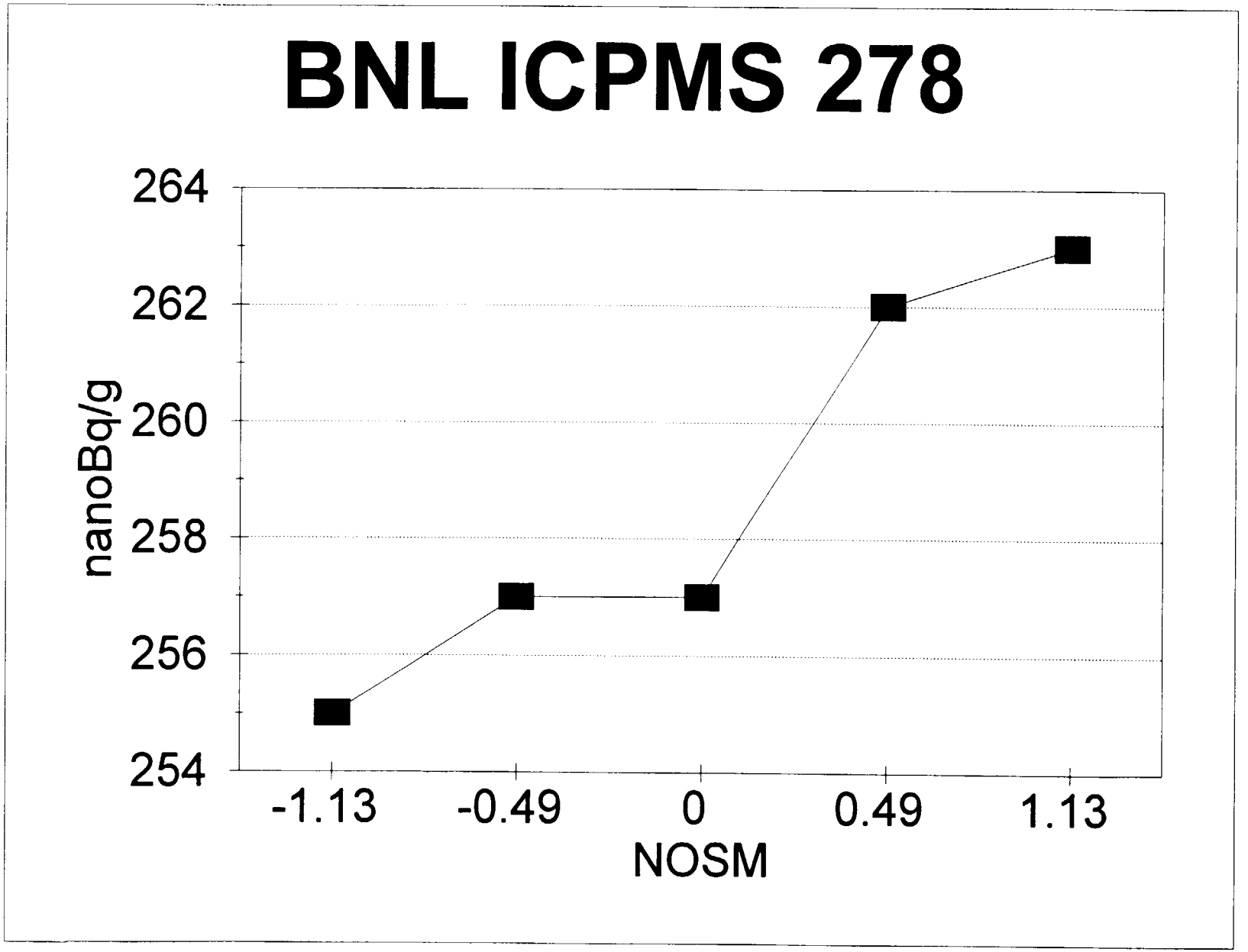

BNL ICPMS BLK
4
2
0
-2
-4
-6
nanoBq/g
-1
-0.5
0
0.5
1
NOSM



94


BNL ICPMS 46
nanoBq/g
44
43
42
41
40
39
38
-1.13
-0.49
0
0.49
1.13
NOSM

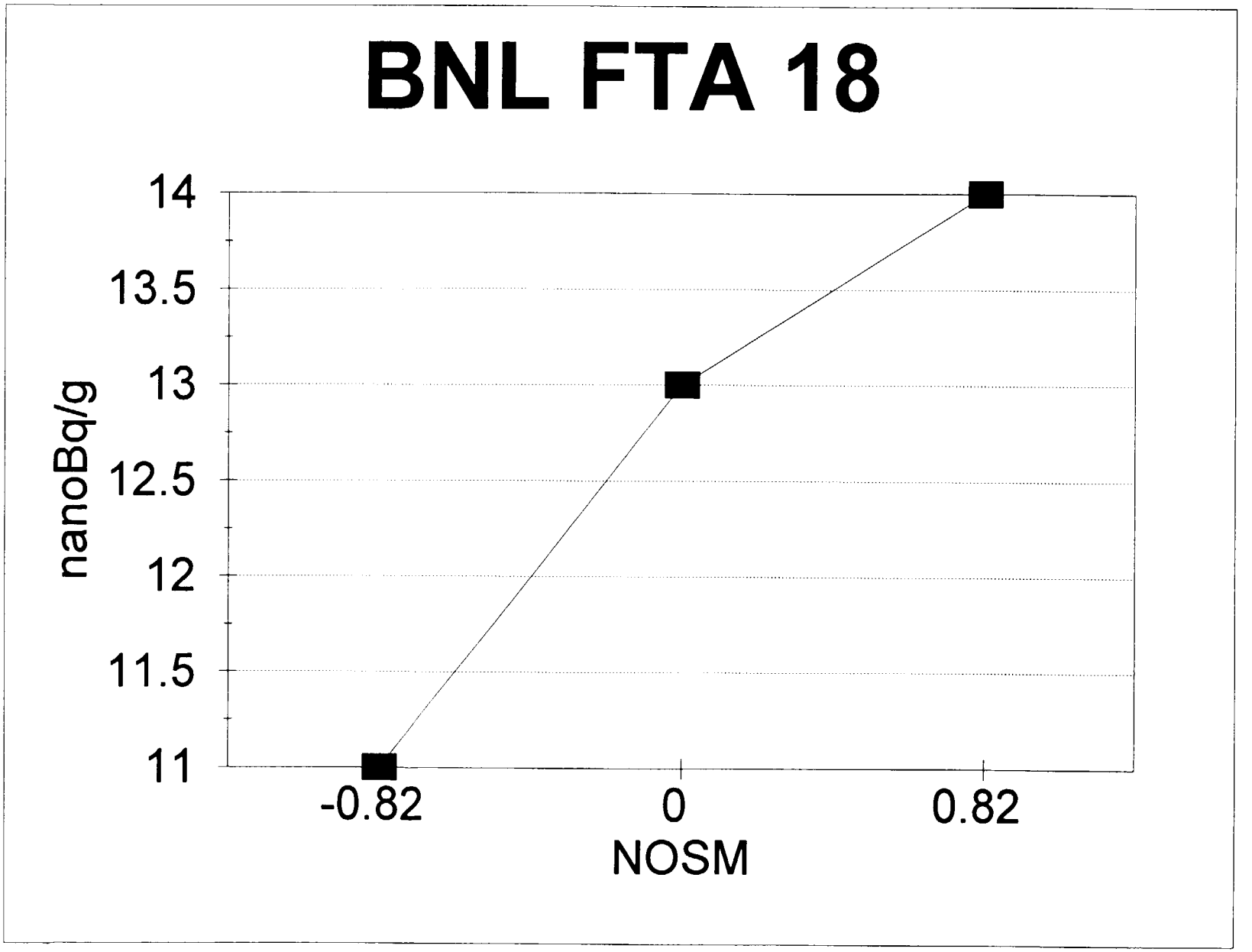

BNL ICPMS 148
138
137
136
135
134
nanoBq/g
-1
-0.29
0.29
1
NOSM


BNL ICPMS 278
264
262
260
258
256
254
nanoBq/g
-1.13
-0.49
0
0.49
1.13
NOSM

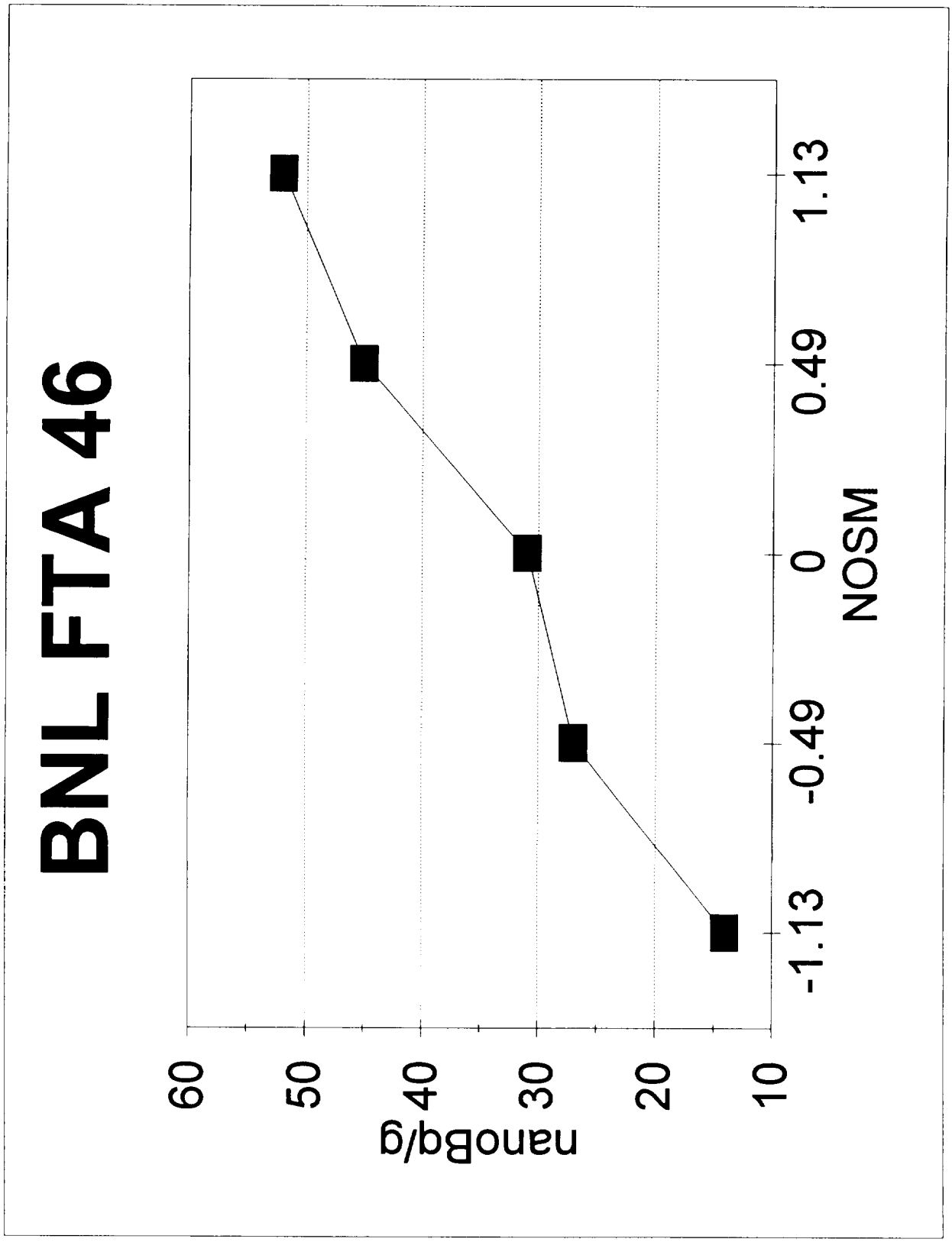
Figures 6-9

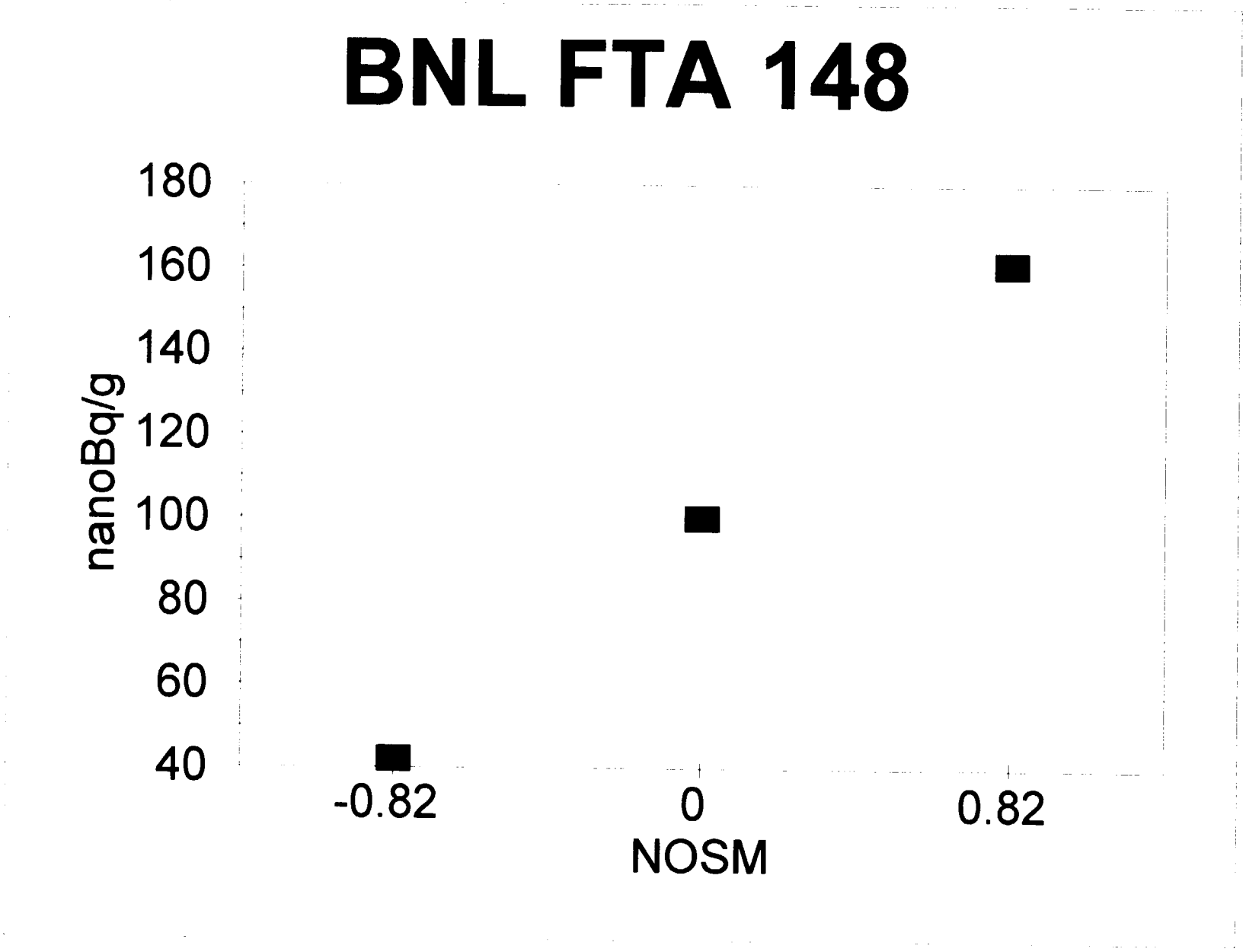
BNL FTA

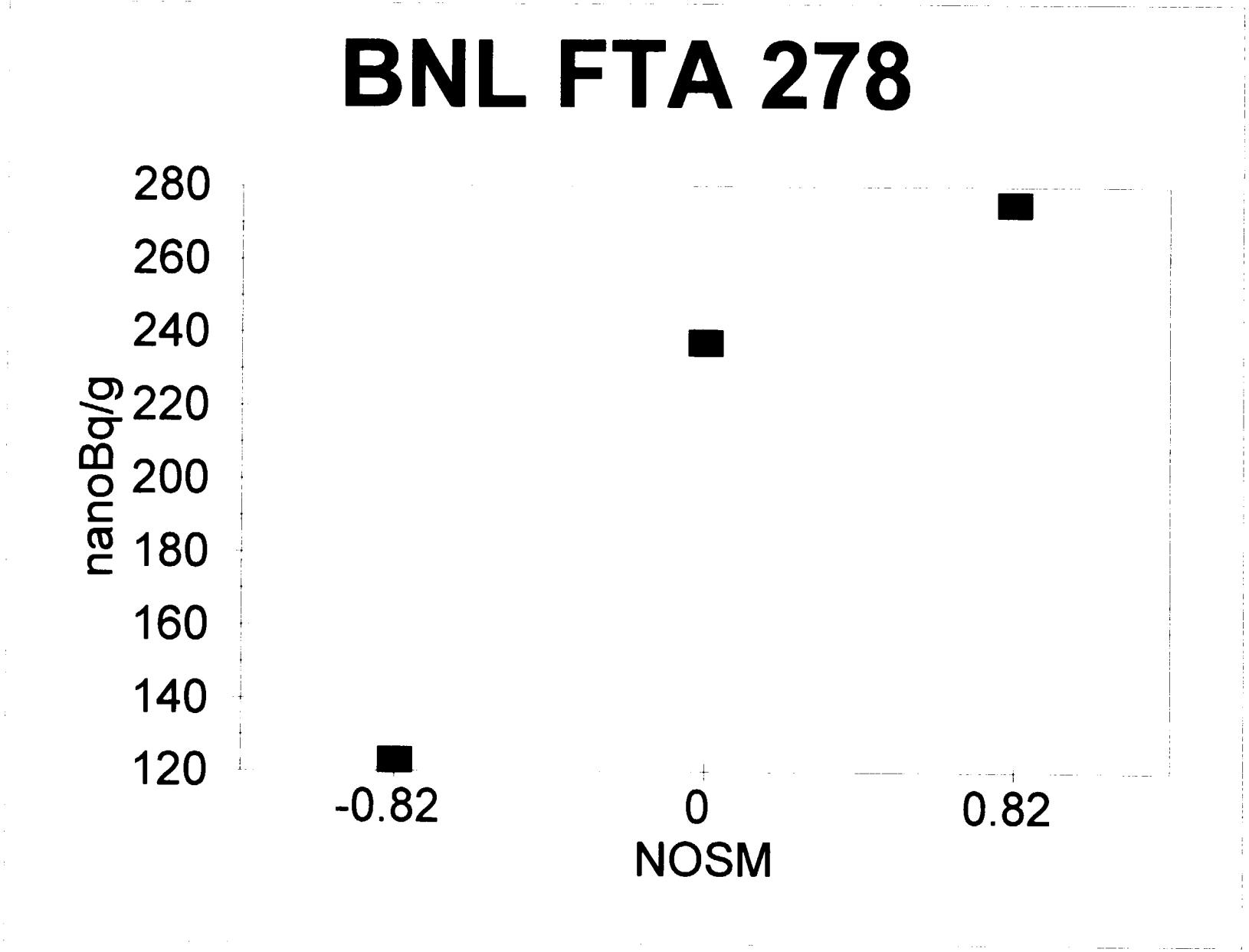
NOSM



bb


BNL FTA 46
nanoBq/g
60
50
40
30
20
10
-1.13
-0.49
0
0.49
1.13
NOSM


BNL FTA 148
180
160
140
120
100
80
60
40
nanoBq/g
-0.82
0
0.82
NOSM

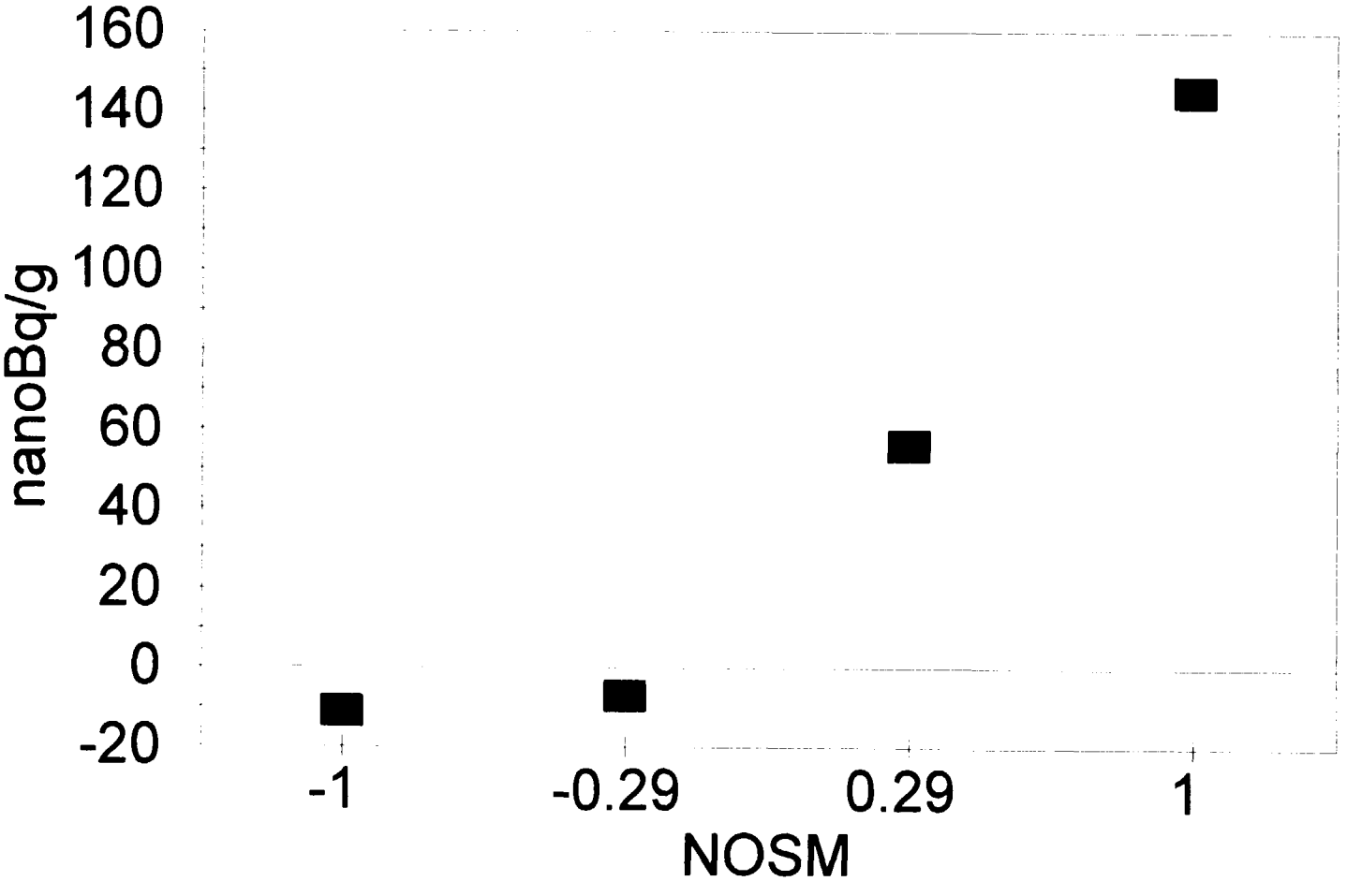

BNL FTA 278
280
260
240
220
200
180
160
140
120
nanoBq/g
-0.82
0
0.82
NOSM

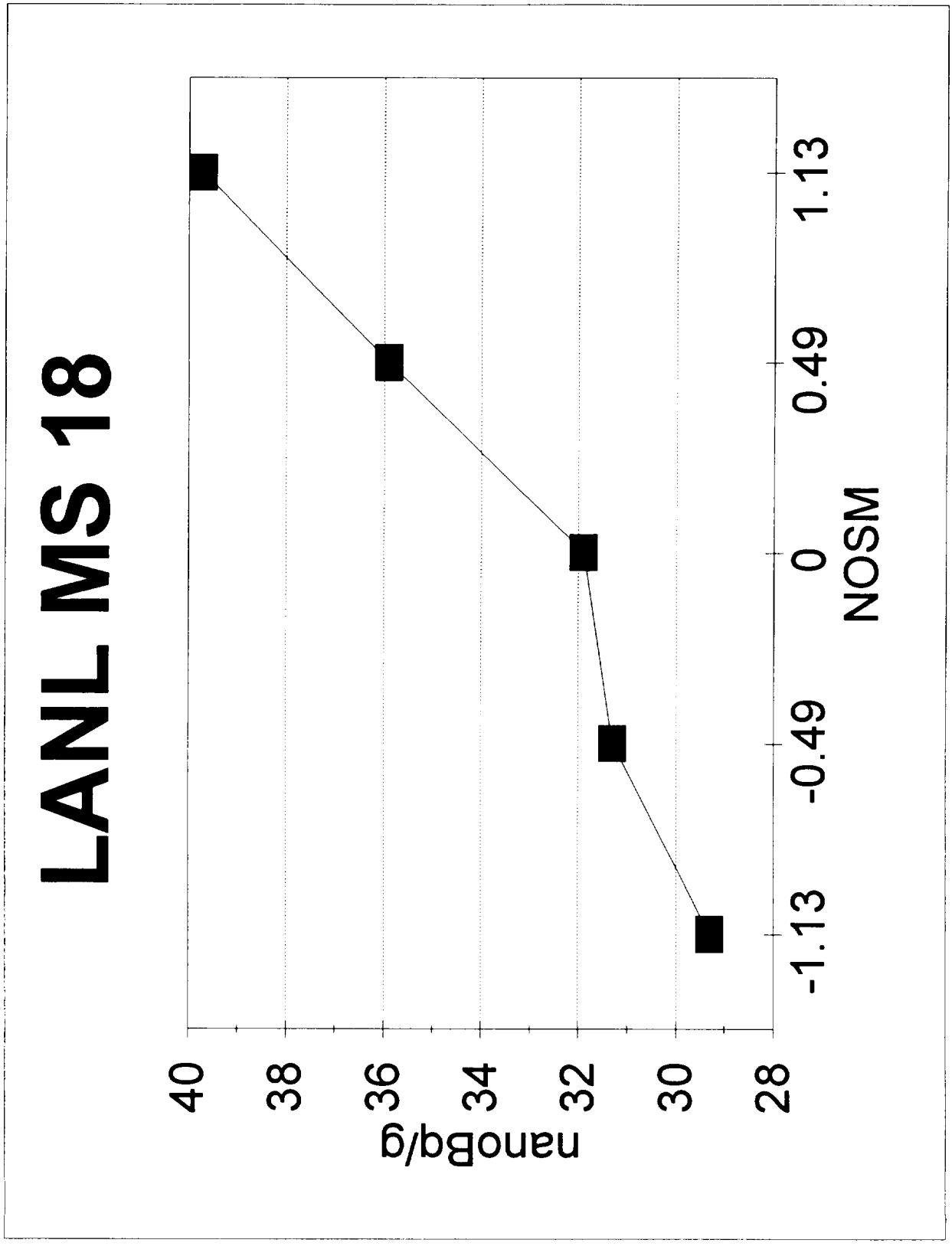
Figures 10-14

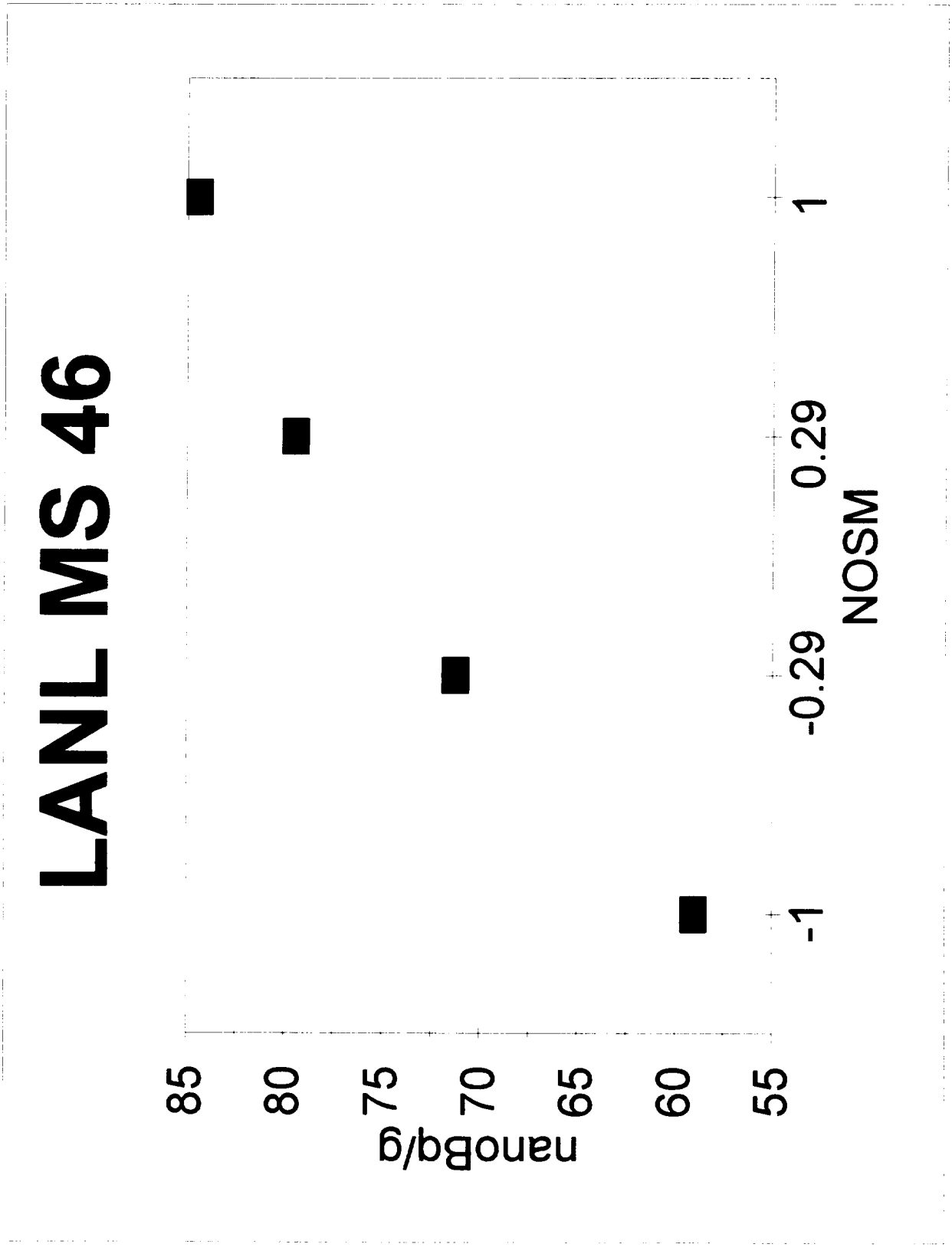
LANL TIMS

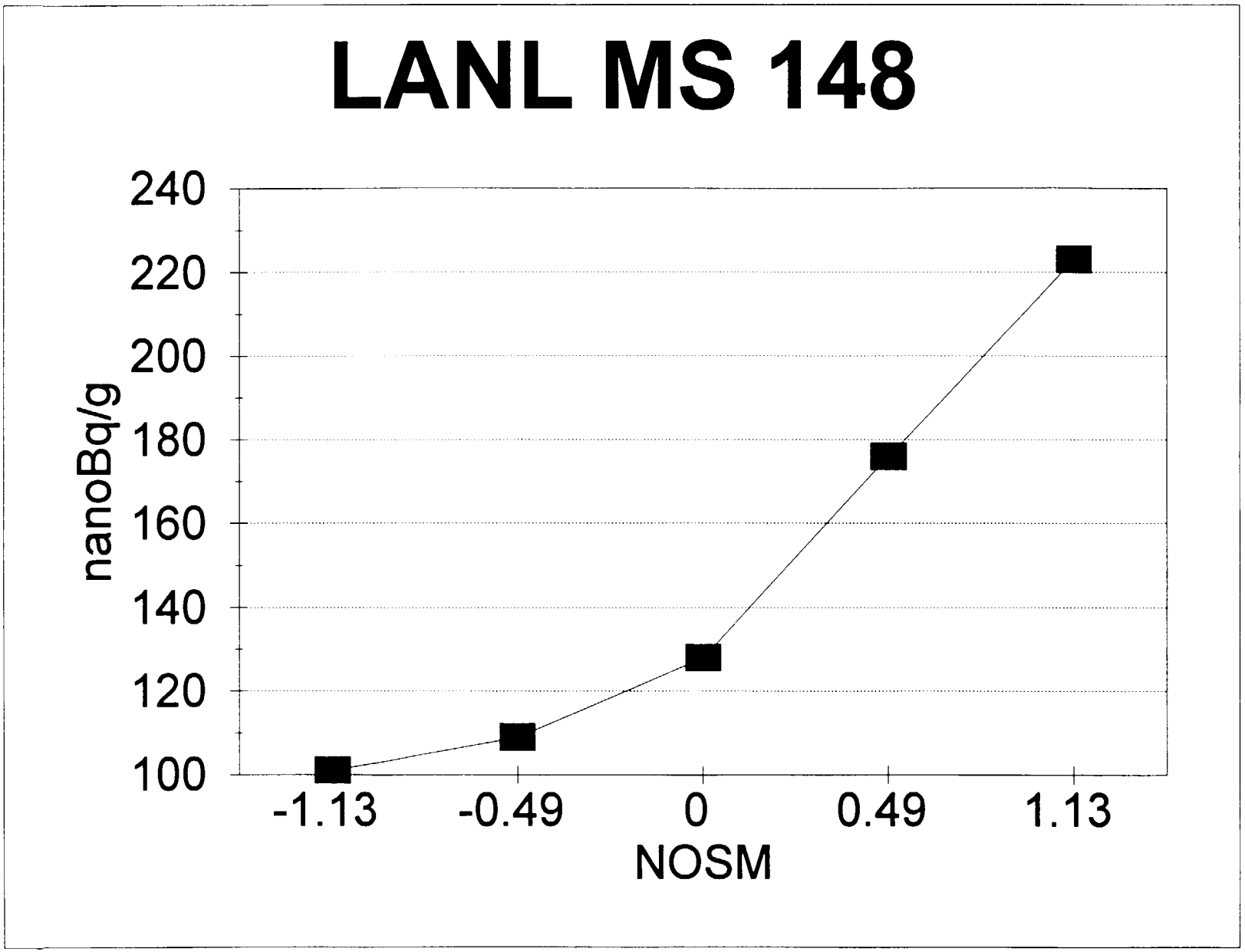
NOSM

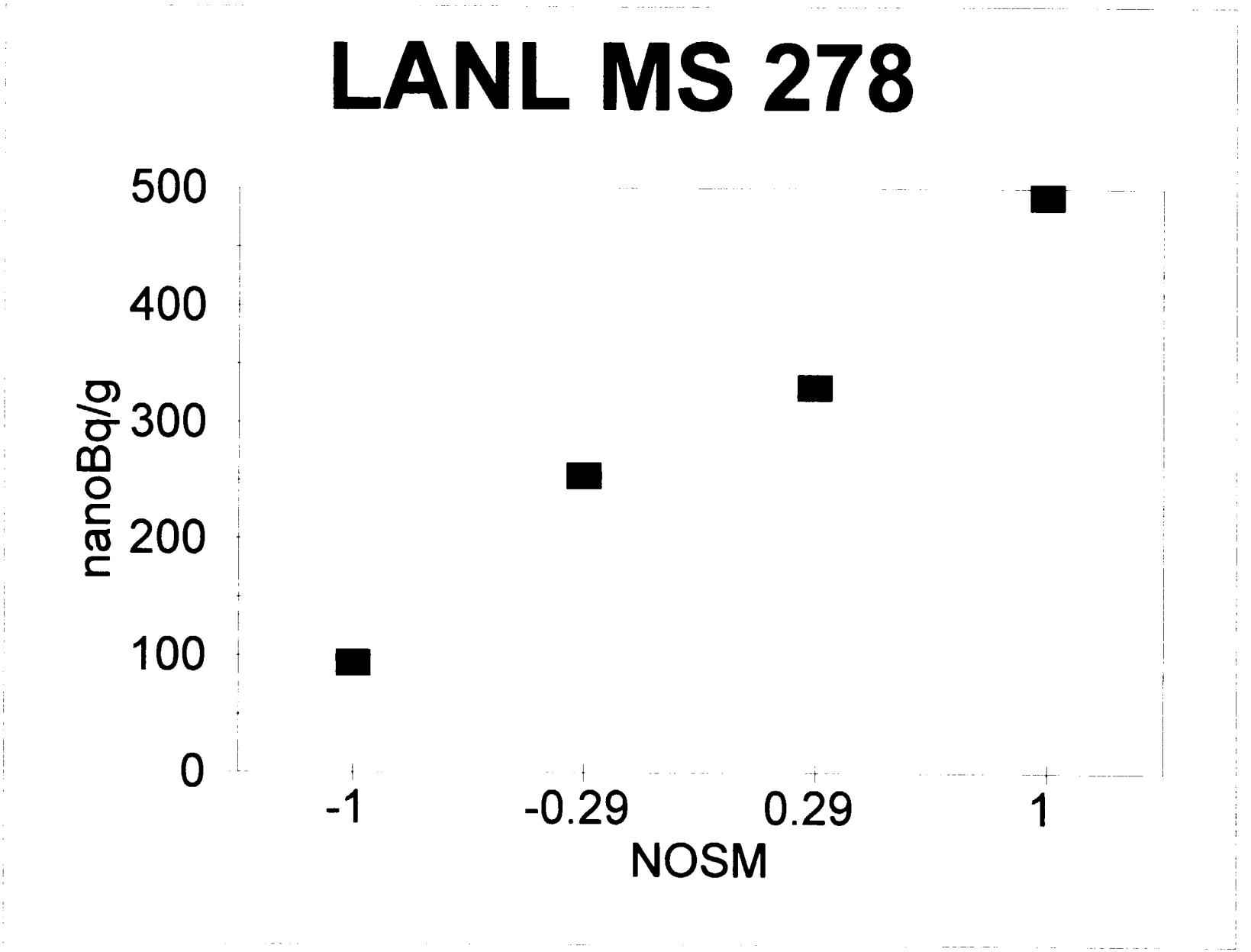
LANL MS BLK




LANL MS 18
nanoBq/g
40
38
36
34
32
30
28
-1.13
-0.49
0
0.49
1.13
NOSM


LANL MS 46
nanoBq/g
85
80
75
70
65
60
55
NOSM
-1
-0.29
0.29
1


LANL MS 148
240
220
200
180
160
140
120
100
nanoBq/g
-1.13
-0.49
0
0.49
1.13
NOSM

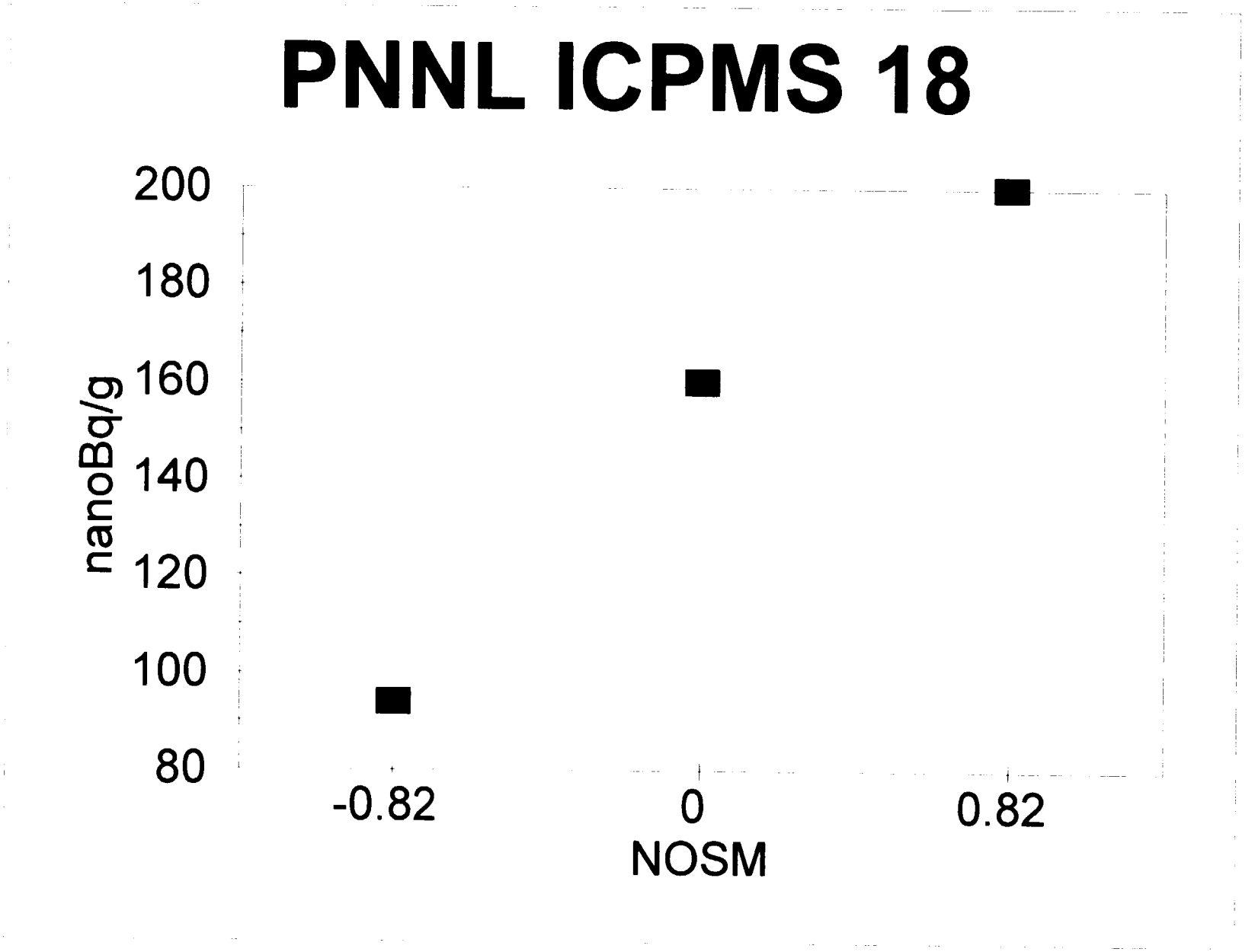


/3 01

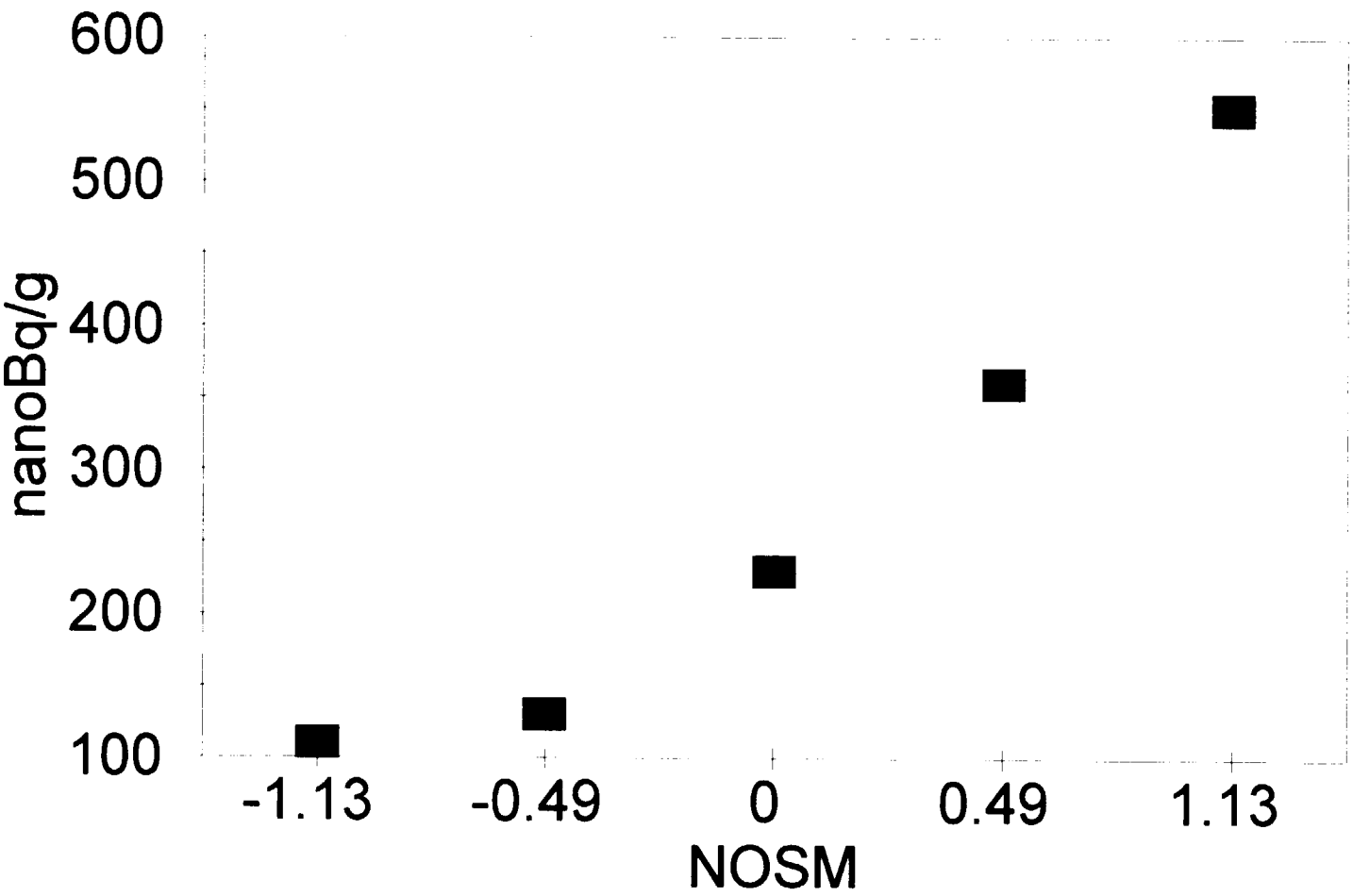
Figures 15-17

PNNL ICP-MS

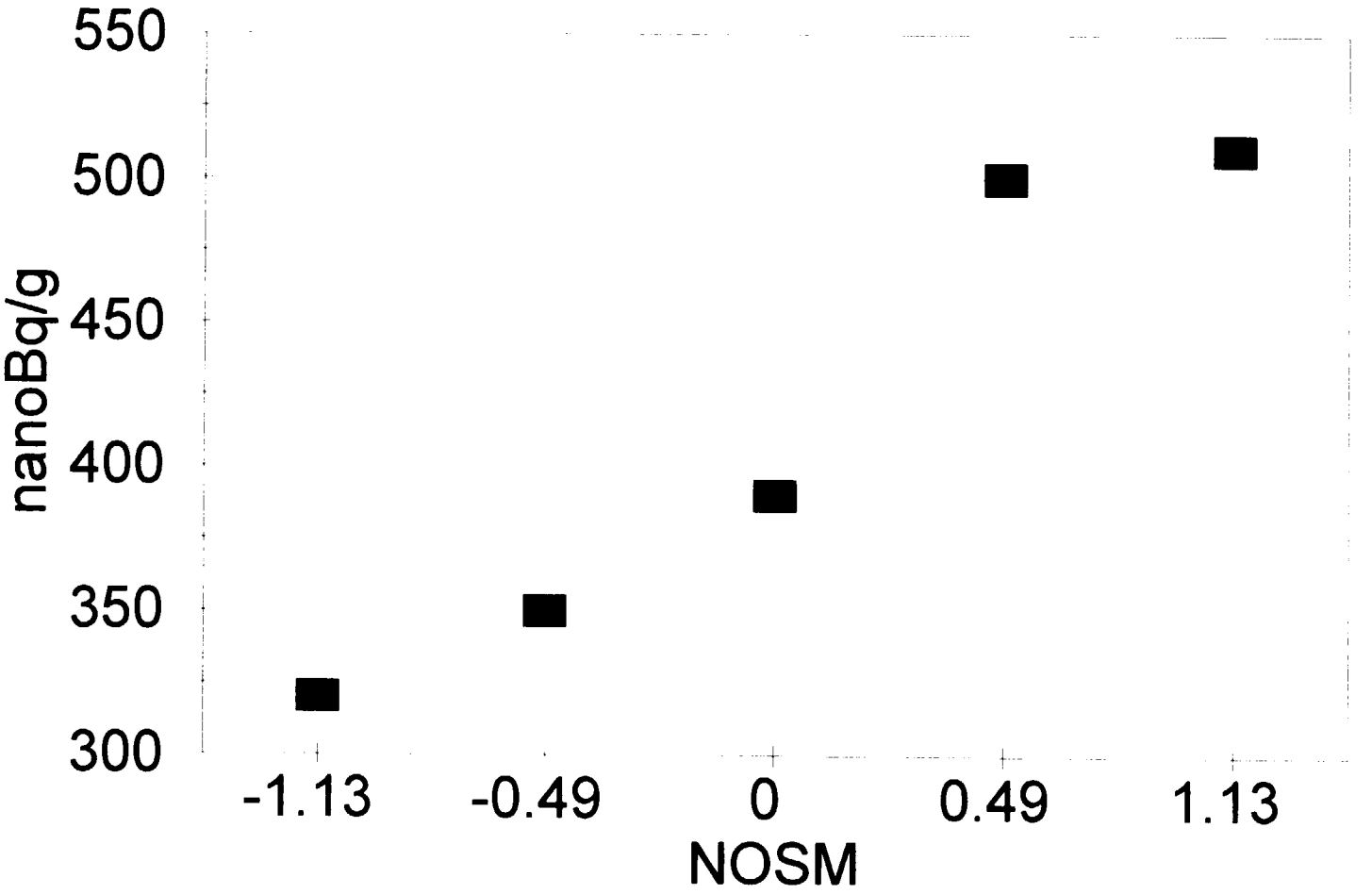
NOSM


PNNL ICPMS 18
200
180
160
140
120
100
80
nanoBq/g
-0.82
0
0.82
NOSM

PNNL ICPMS 148



PNNL ICPMS 278



VI.

REPORT of TRACEABILITY

U.S. Department of Commerce
National Institute of Standards and Technology
Gaithersburg, MD

REPORT OF TRACEABILITY

PLUTONIUM-239

U.S. Department of Energy
International Health Programs, EH-63
Germantown, MD, USA

Test Identification	DOE/EH63/97
Matrix Description	^{239}Pu in synthetic urine solution
Source Description	Solution in glass bottle[1]
Test Concentrations	18.5, 46.3, 148, and 278 $nBq \cdot g^{-1}$
Reference Time	12:00 noon, February 26, 1997

RESULTS:

Per ANSI N42.22 criteria for traceability testing, the results indicate measurements of ^{239}Pu at the testing concentrations were acceptable at the stated uncertainties by:

a) **Brookhaven National Laboratory Inductively Coupled Plasma Mass Spectrometry for the 18, 46, 148 and 278 nBq/g levels;**

b) **Brookhaven National Laboratory Fission Track Analysis for the 18, 46, 148, and 278 nBq/g levels;**

c) **Los Alamos National Laboratory Thermal Ionization Mass Spectrometry for the 148 and 278 nBq/g levels; and**

d) **Pacific Northwest National Laboratory Inductively Coupled Plasma Mass Spectrometry for the 148 and 278 nBq/g levels.**

Per ANSI N13.30 criteria for bias and precision testing, the results indicate measurements of ^{239}Pu at the testing concentrations were acceptable for both criteria by:

a) Brookhaven National Laboratory Inductively Coupled Plasma Mass Spectrometry for the 18, 46, 148 and 278 nBq/g levels;

b) Brookhaven National Laboratory Fission Track Analysis for the 278 nBq/g level;

c) Los Alamos National Laboratory Thermal Ionization Mass Spectrometry for the 148 and 278 nBq/g levels; and

d) Pacific Northwest National Laboratory Inductively Coupled Plasma Mass Spectrometry for the 278 nBq/g level.

Samples distributed **February 28, 1997**
Report received **May 30, 1997**

For the Director

J. M. R. Hutchinson
Group Leader
Radioactivity Group
Physics Laboratory

Fn:kinn/yael/puurine.pap/August 17, 1997

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TEST RESULTS

Nuclide	NIST Values		Reported Value[6] Brookhaven National Laboratory		Difference	ANSI N42.22 Traceable	ANSI N42.22 Traceability Limit[7]	ANSI N13.30 Criteria (Pass/Fail)[8]	
Sample Number ^{239}Pu	nBq per gram[2]	Relative Expanded Uncertainty[3,4,5] ($2s_m$, percent)	nBq per gram	Reported Uncertainty ($2s_m$, percent)	(Percent)		(Percent)	Bias	Precision
PUR100	18.5	1.0	14.7	25	-20	Yes	± 37	Pass	Pass
PUR250	46.3	1.0	40.5	22	-13	Yes	± 33	Pass	Pass
PUR800	148	1.0	136	21	-8.3	Yes	± 32	Pass	Pass
PUR1500	278	1.0	259	21	-6.8	Yes	± 32	Pass	Pass
BLANK	0	-	0.025	12000	-	-	-	-	-

MEASUREMENT TECHNIQUES

NIST	BROOKHAVEN NATIONAL LABORATORY
"0.1π"α defined-solid-angle counter with scintillation detector, 4πα liquid scintillation and high purity germanium counting systems	Inductively Coupled Plasma Mass Spectrometry

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Nuclide	NIST Values		Reported Value[6] Brookhaven National Laboratory		Difference	ANSI N42.22 Traceable	ANSI N42.22 Traceability Limit[7]	ANSI N13.30 Criteria (Pass/Fail)	
Sample Number ^{239}Pu	nBq per gram[2]	Relative Expanded Uncertainty[3,4,5] ($2s_m$, percent)	nBq per gram	Reported Uncertainty ($2s_m$, percent)	(Percent)		(Percent)	Bias	Precision
PUR100	18.5	1.0	12.7	40	-32	Yes	± 60	Fail	Pass
PUR250	46.3	1.0	33.8	55	-27	Yes	± 82	Fail	Pass
PUR800	148	1.0	101	70	-32	Yes	± 105	Fail	Pass
PUR1500	278	1.0	212	57	-24	Yes	± 86	Pass	Pass
BLANK	0	-	5.5	125	-	-	-	-	-

MEASUREMENT TECHNIQUES

NIST	BROOKHAVEN NATIONAL LABORATORY
"0.1π"α defined-solid-angle counter with scintillation detector, 4πα liquid scintillation and high purity germanium counting systems	Fission Track Analysis

Nuclide	NIST Values		Reported Value[6] Los Alamos National Laboratory		Difference	ANSI N42.22 Traceable	ANSI N42.22 Traceability Limit[7]	ANSI N13.30 Criteria (Pass/Fail)	
Sample Number ^{239}Pu	nBq per gram[2]	Relative Expanded Uncertainty[3,4,5] ($2s_m$, percent)	nBq per gram	Reported Uncertainty ($2s_m$, percent)	(Percent)		(Percent)	Bias	Precision
PUR100	18.5	1.0	34	11	82	No	± 17	Fail	Pass
PUR250	46.3	1.0	74	15	59	No	± 23	Fail	Pass
PUR800	148	1.0	147	31	-0.7	Yes	± 47	Pass	Pass
PUR1500	278	1.0	292	57	5.3	Yes	± 85	Pass	Pass
BLANK	0	-	46	160	-	-	-	-	-

MEASUREMENT TECHNIQUES

NIST	LOS ALAMOS NATIONAL LABORATORY
"0.1π"α defined-solid-angle counter with scintillation detector, 4πα liquid scintillation and high purity germanium counting systems	Thermal Ionization Mass Spectrometry

Nuclide	NIST Values		Reported Value[6] Battelle-Pacific Northwest National Laboratory		Difference	ANSI N42.22 Traceable	ANSI 42.22 Traceability Limit[7]	ANSI N13.30 Criteria (Pass/Fail)	
Sample Number ^{239}Pu	nBq per gram[2]	Relative Expanded Uncertainty[3,4,5] ($2s_m$, percent)	nBq per gram	Reported Uncertainty ($2s_m$, percent)	(Percent)		(Percent)	Bias	Precision
PUR100	18.5	1.0	151	61	718	No	± 91	Fail	Pass
PUR250	46.3	1.0	220	101	375	No	± 152	Fail	Fail
PUR800	148	1.0	276	74	86	Yes	± 111	Fail	Pass
PUR1500	278	1.0	414	49	49	Yes	± 72	Pass	Pass
BLANK	0	-	135	69	-	-	-	-	-

MEASUREMENT TECHNIQUES

NIST	BATTELLE-PACIFIC NORTHWEST NATIONAL LABORATORY
"0.1π"α defined-solid-angle counter with scintillation detector, 4πα liquid scintillation and high purity germanium counting systems	Inductively Coupled Plasma Mass Spectrometry

Notes

(1) Five test-sample bottles for each concentration were provided for this test. Each sample consisted of approximately 200 g synthetic urine solution contained in a sealed glass bottle.

Composition of the Synthetic Urine

Component	g/kg
Urea	16.00
NaCl	2.32
KCl	3.43
Creatinine	1.10
Na_2SO_4 (anhydrous)	4.31
Hippuric Acid	0.63
NH_4Cl	1.06
Citric Acid	0.54
$MgSO_4$ (anhydrous)	0.46
$NaH_2PO_4 \bullet H_2O$	2.73
$CaCl_2 \bullet 2H_2O$	0.63
Oxalic Acid	0.02
Lactic Acid	0.094
Glucose	0.48
$Na_2SiO_3 \bullet 9H_2O$	0.071
Pepsin	0.029
Conc. Nitric Acid	50.00
Yellow Food Color (optional)	0.06

(2) Gravimetric dilutions of Standard Reference Materials were confirmed by replicate (n=5, at each concentration level) radioactivity measurements.

(3) The analysis methodology and nomenclature used for the reported uncertainties for NIST values are based on uniform guidelines [cf., B.N. Taylor and C. E. Kuyatt, NIST Technical Note 1297 (1994)] and are compatible with those adopted by the principal international metrology standardization bodies. Individual uncertainties have the significance of one standard deviation of the mean, or an approximation thereof. The relative combined uncertainty, u_c, is the quadratic combination of the standard deviation (or standard deviation of the mean where appropriate), or approximation thereof, for the following component uncertainties:

	Source of Uncertainty	Uncertainty
a)	Gravimetric measurement	0.35 percent
b)	^{239}Pu certified uncertainties	0.36 percent

The individual certified uncertainties of standard reference materials are based on the quadratic combination of all sources of uncertainty manifest in the preparation the material. These uncertainties may result from uncertainties from any or all of the following: alpha-decay emission rate, background, balance calibration, decay corrections, decay-scheme data, extrapolation of alpha-particle-count-rate-versus-energy to zero energy, live time, alpha-particle detection efficiency, alpha-emitting impurities, gamma-emitting impurities.

The relative expanded uncertainty, U, is obtained by multiplying u_c by a coverage factor of k=2 and is assumed to provide an uncertainty interval of approximately 95 percent confidence.

(4) Impurities (SRM 4330A solution) none detected

Estimated limits of detection for photon-emitting impurities are:
2.00×10^{-4} $\gamma \cdot s^{-1}$ for energies between 42.5 and 90 keV,
8.0×10^{-5} $\gamma \cdot s^{-1}$ for energies between 102 and 125 keV,
3.0×10^{-6} $\gamma \cdot s^{-1}$ for energies between 133 and 1456 keV,
8×10^{-6} $\gamma \cdot s^{-1}$ for energies between 1465 and 3500 keV,
Provided that the photons are separated in energy by 4 keV or more from photons emitted in the decay of plutonium-239.

Alpha-emitting impurities (SRM solution) none detected

Estimated limits of detection for alpha-particle-emitting impurities are:
0.04 $\alpha \cdot s^{-1}$ for energies less than 4.9 MeV and
0.001 $\alpha \cdot s^{-1}$ for energies greater than 5.2 MeV.

From mass-spectrometric measurements performed by the supplier, the massic activity ratios of other detected radionuclides (at 1200 EST, 4 December 1995) are:
$^{239}Pu/^{239}Pu$: 5.3×10^{-5}
$^{241}Pu/^{239}Pu$: 5.3×10^{-4}
$^{242}Pu/^{239}Pu$: 7.9×10^{-8}
$^{241}Am/^{239}Pu$: 2.0×10^{-5}

(5) Half-life ^{239}Pu 24119 ± 26 years

(6) Test results were evaluated based upon reported measurements. Values from results associated with low chemical yield, below detection limits, and outlier test of normal distribution were not included in the evaluations.

(7) ANSI N42.22 defines the traceability limit to NIST for performance testing as:

$$|V_N - V_L| \leq 3 * \sqrt{(\delta_N^2 + \delta_L^2)}$$

Where: V_N = NIST Value;

V_L = Laboratory Value;

δ_N = 1 sigma total uncertainty of the NIST value, V_N; and

δ_L = 1 sigma total uncertainty of the Laboratory value, V_L.

(8) ANSI N13.30 defines criteria for acceptable bias between -25 to +50 percent, and acceptable precision between -40 to +40 percent, 1 sigma total propagated uncertainty.

Information contacts: Dr. Kenneth G. W. Inn (301) 975-5541

References:

ANSI National Standards Institute, ANSI N42.22-1995, "Traceability of Radioactive Sources to the National Institute of Standards and Technology (NIST) and Associated Instrument Quality Control."

ANSI National Standards Institute, ANSI N13.30-1996, "Performance Criteria for Radiobioassay."

VI.

ANALYTICAL ISSUES

Analytical Problems

Aside from misidentified samples and computation errors, this study revealed the following analytical problems:

Analytical Bias - Generally, biases approaching 5 percent are observed for the higher concentration test samples. It is likely that the accuracy of the chemical yield monitors (tracers) is a considerable portion of this bias. Careful preparation of yield monitors should remove most of the analytical bias. In addition, FTA is handicapped with a serious bias limitations when track density is high, and when batch chemical yield corrections are used. These sources of error severely limit FTA from being capable of being improved.

Uncertainties - BNL FTA, LANL TIMS and PNNL ICP-MS relative uncertainties increased with increasing plutonium concentration - This is contrary to intuition and should be investigated for root cause by each laboratory.

Imprecision - Most of the poor precision is caused by high variable blanks and low chemical yield (see below). Large measurement uncertainty could result in failing the ANSI N13.30 criteria for precision.

High Variable Blank - LANL and PNNL's results suffered from high and variable blanks. BNL ICP-MS results, by contrast, had very low and consistent blanks. Presumably, BNL has developed extreme sensitivity to sample and reagent contamination, and have developed extraordinary cleanroom techniques and ultra-pure reagents for analysis. The results of this study indicate that BNL's successes is strongly linked to their ability to control and minimize any blank contributions. LANL and PNNL should undertake careful study of their analytical system to seek out and control sources of contamination.

Low Chemical Yield - Discussions with the investigators indicated that chemical yields for natural urine samples are typically in the 70-80 percent range. The synthetic urine used in this study caused chemical yields to occasionally decrease to 20 percent. The root cause should investigated, particularly because it causes this technology evaluation to be inaccurate (particularly the evaluation of precision and MDA), and because the radiobioassay DOELAP effort will use the synthetic urine as the test matrix.

Lost Data - 21 percent of the reported results were not included in the study because of <MDA, analytical outlier, poor precision, overlapping tracks, or even poor reliability. This fraction is unacceptably high for production line operations. The reliability of the analytical systems must be improved through systematic

methods evaluations at each participating laboratory and brought under statistical control. Presumably, highly experienced analysts would be used to analyze the DOE-Marshall Islander urine samples because of the program's high political profile.

Study Limitation

A serious limitation to this study is the absence of important isobaric and chemical interferences in the synthetic urine matrix. Addition of interferences would have also tested chemical separations and measurement selectivity. Interference that are present in natural urine include calcium, iron, lead, uranium and thorium isotopes, ^{240}Pu and ^{241}Pu. The results of this study should be interpreted as being collected under optimum conditions. Including interferences would have more closely simulate analytical performance on natural urine.

In spite of these study shortcomings, sufficient data exists to address the underlying objectives of this study, and will be provided in the next section.

VII.

STATE-of-the-ART

Precision

Total Propagated Uncertainties (K=3) are displayed in Figures 18-22. BNL ICP-MS had the best precision among all of the measurements. LANL TIMS, and even more so for PNNL ICP-MS, had poorer precision (by factors of about 1.5 and 4, respectively). It is likely that superb analytical blank control by BNL played a key role in their excellent performance for measurement precision. Although both LANL and PNNL ran internal blank controls, their results for the unspiked samples indicated additional sources of contamination.

BNL FTA's precision was 2-3 times poorer than for ICP-MS. This is because there are inherent precision limitations for FTA: a) when there are few tracks, track resolution is good, but there is poor statistics, and b) when there are many tracks, track resolution is poor, and precision and bias are adversely affected. These drawbacks, in part, account for the increasing uncertainty as plutonium concentration increased.

It is unclear at this time why the LANL TIMS and PNNL ICP-MS relative measurement precision increased as the plutonium concentration increased. In general, the reverse is expected because of higher ion fluxes. This point is left for future investigations.

Bias

Figures 23-27 displays the percent bias at each ^{239}Pu concentration level. Interpretation of these results are complicated by measurements with poor precision. However, the clear message is that BNL ICP-MS has the best set of bias values. BNL ICP-MS results make an unambiguous statement of its terrific measurement capabilities for ^{239}Pu at the μBq level with its excellent accuracy and measurement precision. The excellent agreement with the NIST values lends support to the presumption that the test samples were stable and accessible during this exercise. The BNL ICP-MS value for the blank samples was extremely low, and was probably responsible for the good performance. It is noted, however, that there is a systematic negative bias. It will have to be left to future investigations to determine if the negative bias is due to a systematic difference in the certification of the ^{242}Pu tracer.

LANL TIMS had serious bias problems at the 18.5 and 46.3 nBq/g levels. However, excellent bias values were obtained at the 148 and 278 nBq/g levels, although with poorer precision. None-the-less, these results illustrate the potential for TIMS to improve and be competitive with ICP-MS. To improve its performance, LANL should begin addressing the unaccounted blank contamination.

PNNL ICP-MS bias steadily worsened as concentration levels dropped. These results are probably strongly linked to the extremely high value they observed from the blank samples. There is no technical reason to prevent PNNL from achieving the same

performance capabilities as BNL ICP-MS.

The BNL FTA bias is larger than those from ICP-MS, but are somewhat better than LANL at the lower concentrations and poorer at higher concentrations. As mentioned before, the poorer FTA performance is related to track density. It would be possible for BNL FTA to improve its bias performance when internal tracers (chemical yield monitors) are used. The results of this study indicates that FTA can make measurements within about 80 percent of a true value, 99.7 percent of the time, over the ^{239}Pu 3.7-55.6 µBq range.

ANSI Performance Criteria

All four laboratories demonstrated their ability to make traceable measurements, per ANSI N42.22 criteria, at the 148.4 and 277.7 nBq/g concentration levels. At the 18.5 and 46.3 nBq/g concentration level, however, only BNL's ICP-MS and FTA measurements were traceable. The FTA success at making traceable measurements at the lower concentration levels, however, was primarily due to relatively large total propagated uncertainties.

All four laboratories passed both the precision and bias ANSI N13.30 criteria at the 277.7 nBq/g level. Only BNL's ICP-MS passed the ANSI N13.30 criteria for all four concentration levels.

Minimum Detectable Amount (MDA)

The estimated MDAs were derived from the ANSI N13.30 equations; the simplified equation, MDL = $4.65s_b + 3$, was not used because of significant contributions from systematic biases.

The general MDA equation from ANSI N13.30, when α and β are equal, is:

$$MDA \quad \frac{(1 \pm \Delta_K)\,(2\Delta_B B \pm 2ks_0 + 3)}{KT} \qquad \text{(Eq 6)}$$

where:

- B = the total count of the appropriate blank,
- s_0 = the standard deviation in the net sample count of a subject with no additional analyte, defined by ANSI N13.30 Equation 2,
- K = calibration factor, (including correction for self absorption when appropriate),
- Δ_K = the maximum fractional systematic error bound in the calibration factor K, (like Δ_B, Δ_K cannot be estimated using replicate measurements, and must be estimated by the professional judgment of the analyst),
- Δ_B = the maximum expected fractional systematic error bound in the

appropriate blank, (The factor of 2 before the Δ_B takes into account the maximum systematic error bound when the background and sample measurement errors are of opposite sign),

k = the abscissa of the standardized normal distribution corresponding to the 0.05 probability level, for $\alpha = 0.05$ and $\beta = 0.05$, k = 1.645,

T = standard subject counting time for the procedure.

The MDA can be obtained from data in units of count-rate from:

$$MDA = (1 + \Delta_K')(2\Delta_B B' + 2ks_0' + 3)/K' \qquad \text{(Eq 7)}$$

where:

$B' = B/T$

$s_0' = s_0/T$

$K' = K/T$

$\Delta_k' = \Delta_k$ since they represent the same fractional systematic relative fixed error.

The unprimed quantities are used when total counts are used in the computation, and the primed quantities are used when the count rates are computed.

For this exercise, equation 7 was used to calculate MDAs. It was further assumed that $\Delta_k' = \Delta_B$. Because several blank sample results were not reported, and estimated uncertainties for the blank sample results were large, an extrapolation method was chosen to improve the reliability of estimating MDA's. MDA's were calculated on Spreadsheet 5 at each concentration level, and extrapolated back to "0" nBq/g (see Figures 30-33). BNL ICP-MS MDA's were fairly reproducible across the entire concentration range, the reported MDA for this study is the mean value, and the CI is reported as two standard deviations of the calculated MDA's. The estimated MDA's for the 200 g sample are as follows:

Laboratory	MDA (nBq/200g sample)	95% Confidence Interval (Percent)
BNL ICP-MS	1600	35
BNL FTA	1200	1900
LANL	600	590
PNNL	91000	3600

In general, routine alpha spectroscopy's MDA is about 3 x 10^6 nBq. These results indicate that mass spectroscopy's (BNL ICP-MS and LANL TIMS) MDA is about 3000 times lower than for alpha spectroscopy. This is in contrast to the study by Lee et al (Bioassay Procedures for Neptunium-237, S.C. Lee, J.M.R. Hutchinson, K.G.W. Inn, and M. Thein, Health Physics, 68 (3), 350-358, 1995; An Intercomparison Study of Neptunium-237 Determination in Artificial Urine Samples, J.M. Robin Hutchinson, Shan Lee, and Kenneth G.W. Inn, Report to DoE DE-AIO5-91OP21969, May 1993) where they found ICP-MS only had comparable measurement capabilities to alpha spectroscopy for ^{239}Np in synthetic urine. FTA's MDA is comparable to that expected from mass spectroscopy, but is a factor of 10-100 times less certain.

The best MDA's were obtained by BNL's ICP-MS and LANL's TIMS. Although the estimated BNL MDA is somewhat larger than LANL's, it is known with much better precision and confidence. The estimated BNL FTA and PNNL ICP-MS MDAs were determined with only poor precision.

Summary

The results of this study revealed the current potential of the ICP-MS, TIMS, and FTA capabilities. These are summarized in Spreadsheet 6. It is apparent that mass spectrometry is currently capable of successfully competing with FTA's sensitivity, and at considerably higher precision down to the 3.7 µBq/sample level. In addition, mass spectrometry has the potential to improve with new technology (e.g., new nebulizer design, multi-pulse detection systems, selective laser ionization) to provide more accurate and precise measurements than FTA. Chemical technologies can be improved with robotics, and the savings in terms of human resources can be shared by all three measurement

technologies. However, mass spectroscopy can eventually become more cost effective than FTA because of quicker turnaround times. ICP-MS, has apparently closed the precision gap with TIMS, and is very competitive with regards to accuracy and precision.

In summary:

- ICP-MS results indicated the tremendous potential to accurately and precisely measure μBq quantities of ^{239}Pu in synthetic urine, while maintaining competitive sensitivity (MDA) with FTA.

- FTA can also measure μBq quantities of ^{239}Pu in synthetic urine, but with considerably larger uncertainty than mass spectroscopy.

- TIMS also has the potential to also overtake FTA's measurement capabilities, but must make a considerable effort to identify and control root causes of high blanks and imprecision.

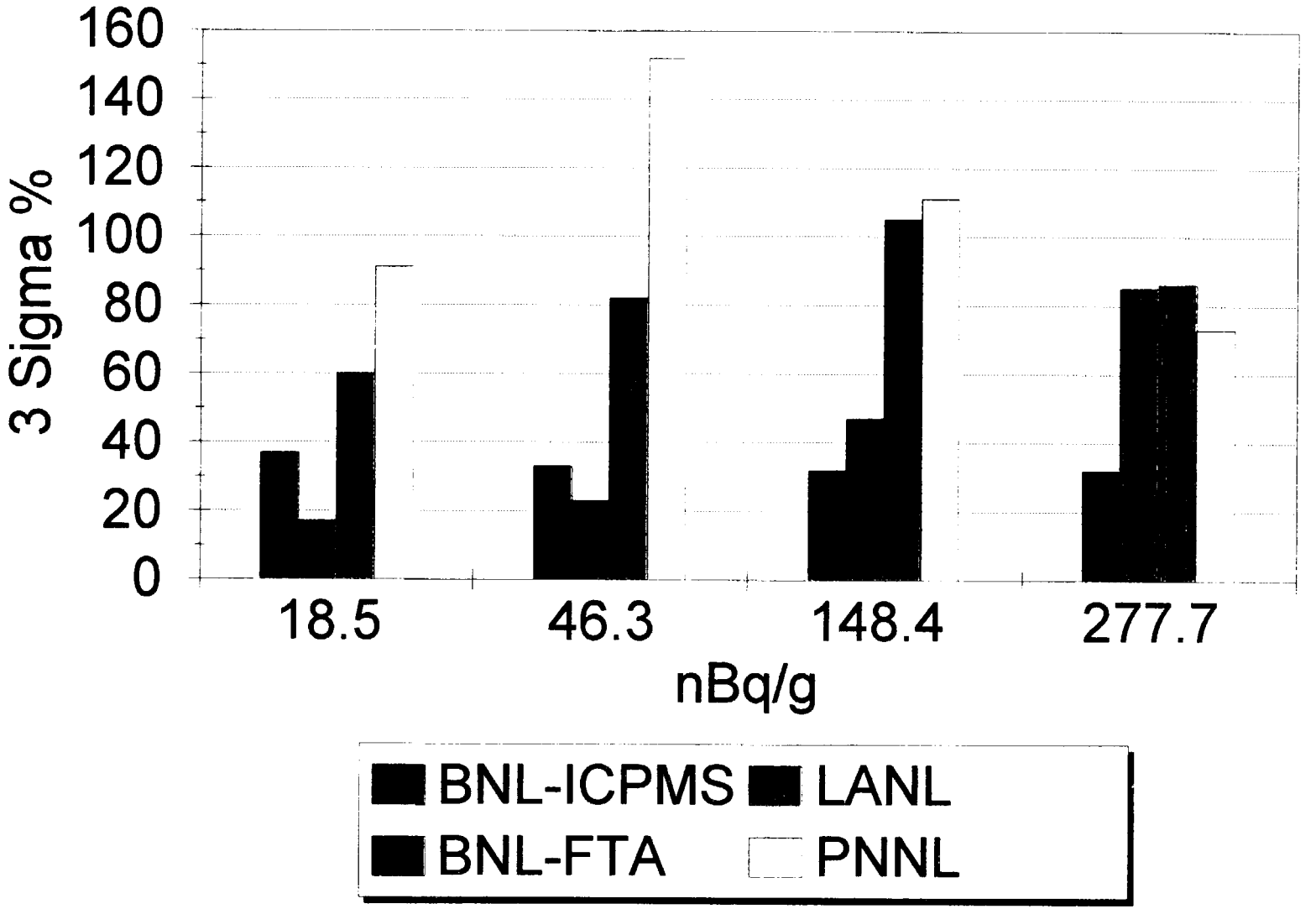
- Controlling analytical blank is crucial for measuring ultra-low levels of ^{239}Pu in urine, which also means careful and exhaustive chemical separations cannot be avoided.

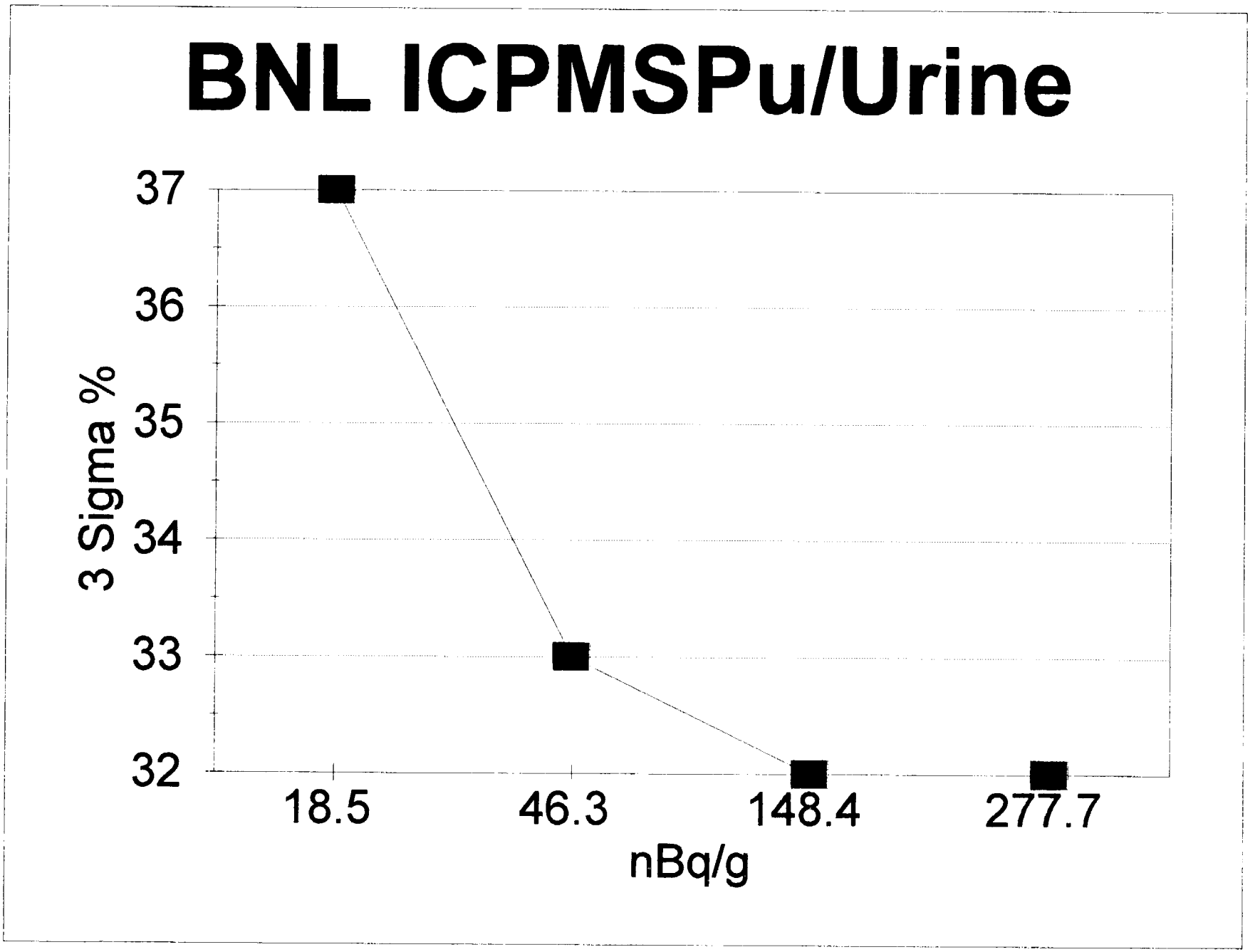
- The chemists must find ways to improve chemical yields to improve measurement sensitivity and reliability.

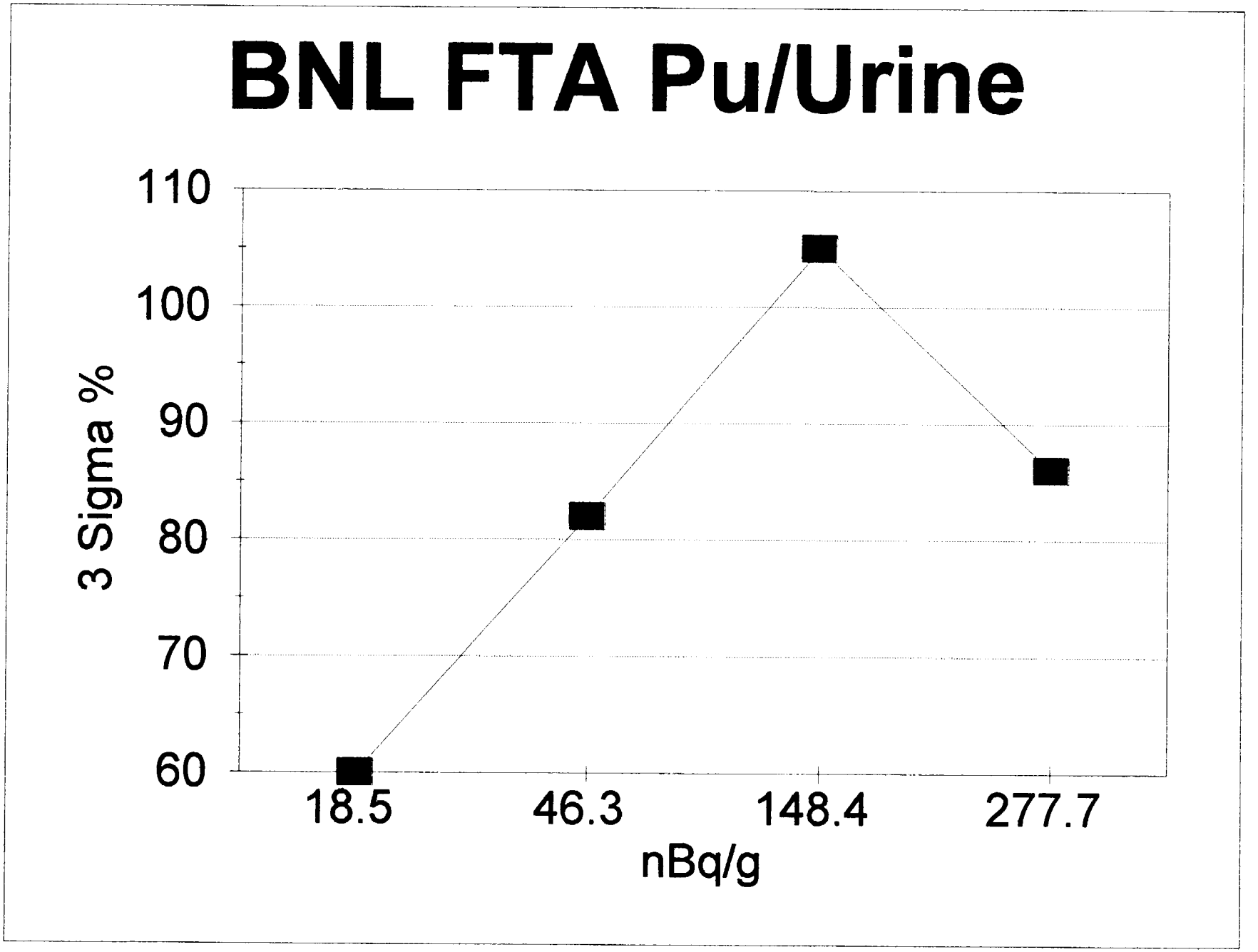
Figures 18-22

Total Propagated Uncertainties

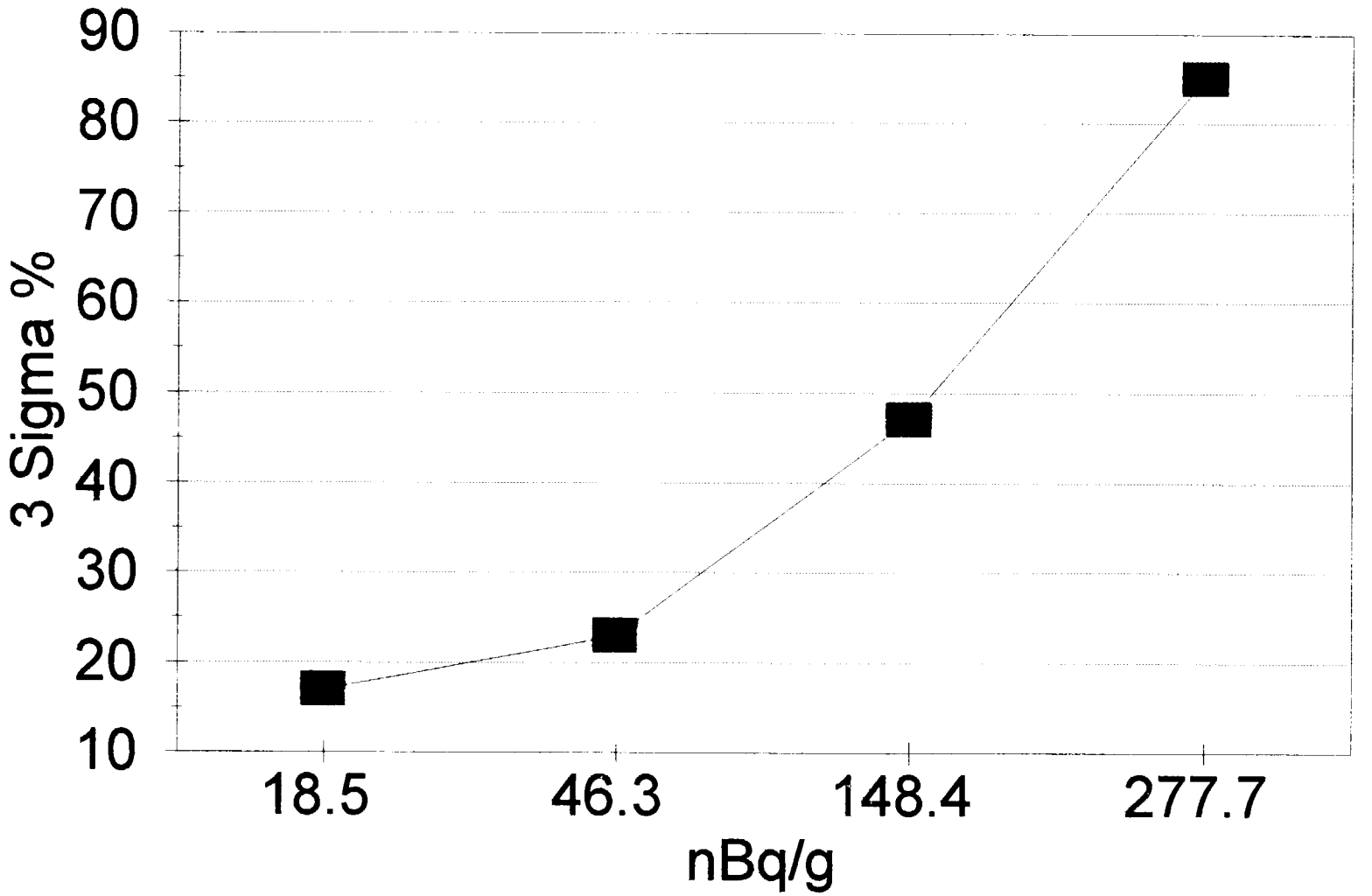
Pu in Urine


160
140
120
100
80
60
40
20
0
3 Sigma %
18.5
46.3
148.4
277.7
nBq/g
BNL-ICPMS
LANL
BNL-FTA
PNNL


BNL ICPMSPu/Urine
37
36
35
34
33
32
3 Sigma %
18.5
46.3
148.4
277.7
nBq/g

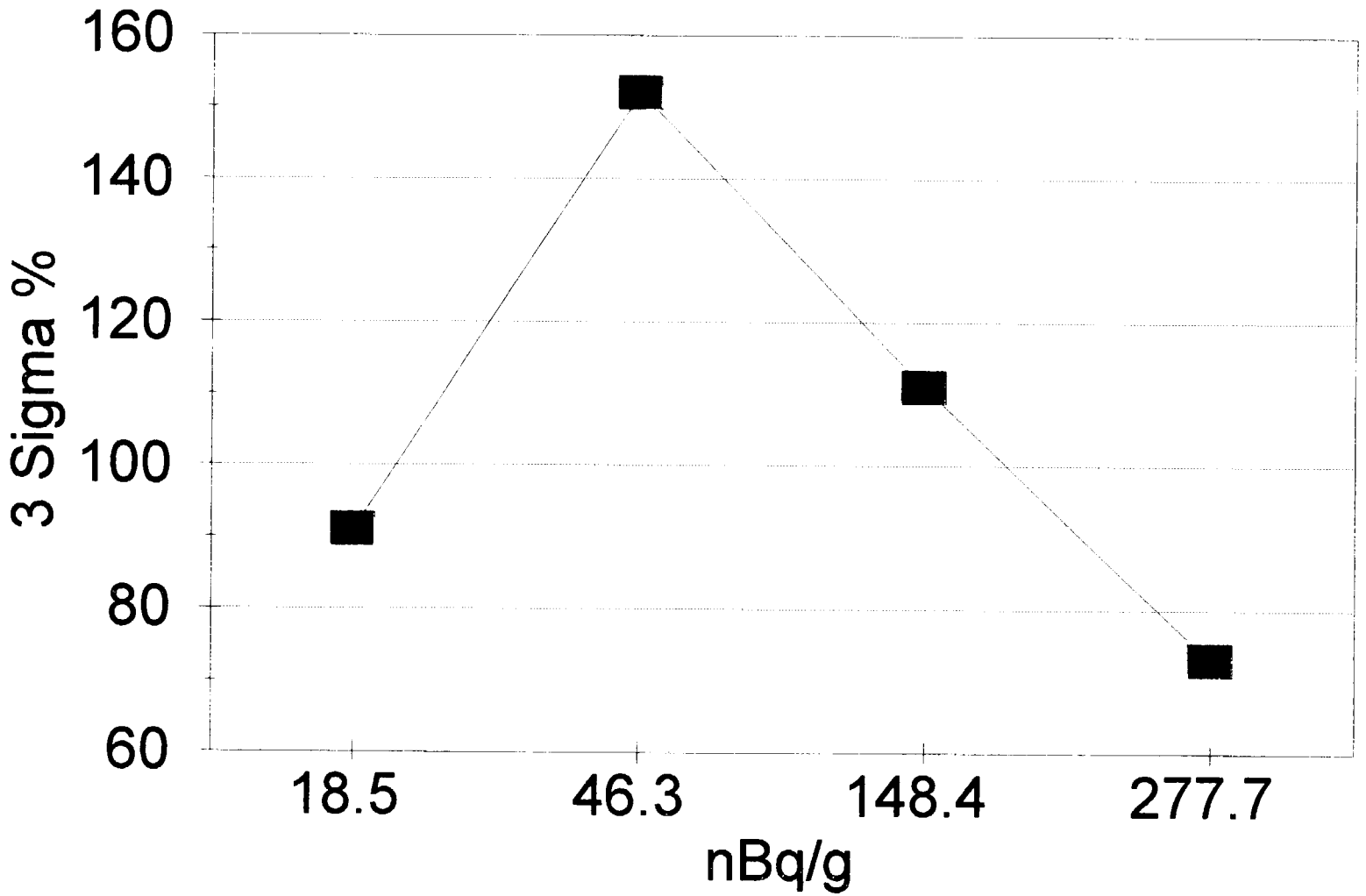

BNL FTA Pu/Urine
110
100
90
80
70
60
3 Sigma %
18.5
46.3
148.4
277.7
nBq/g

LANL TIMS Pu/Urine



136

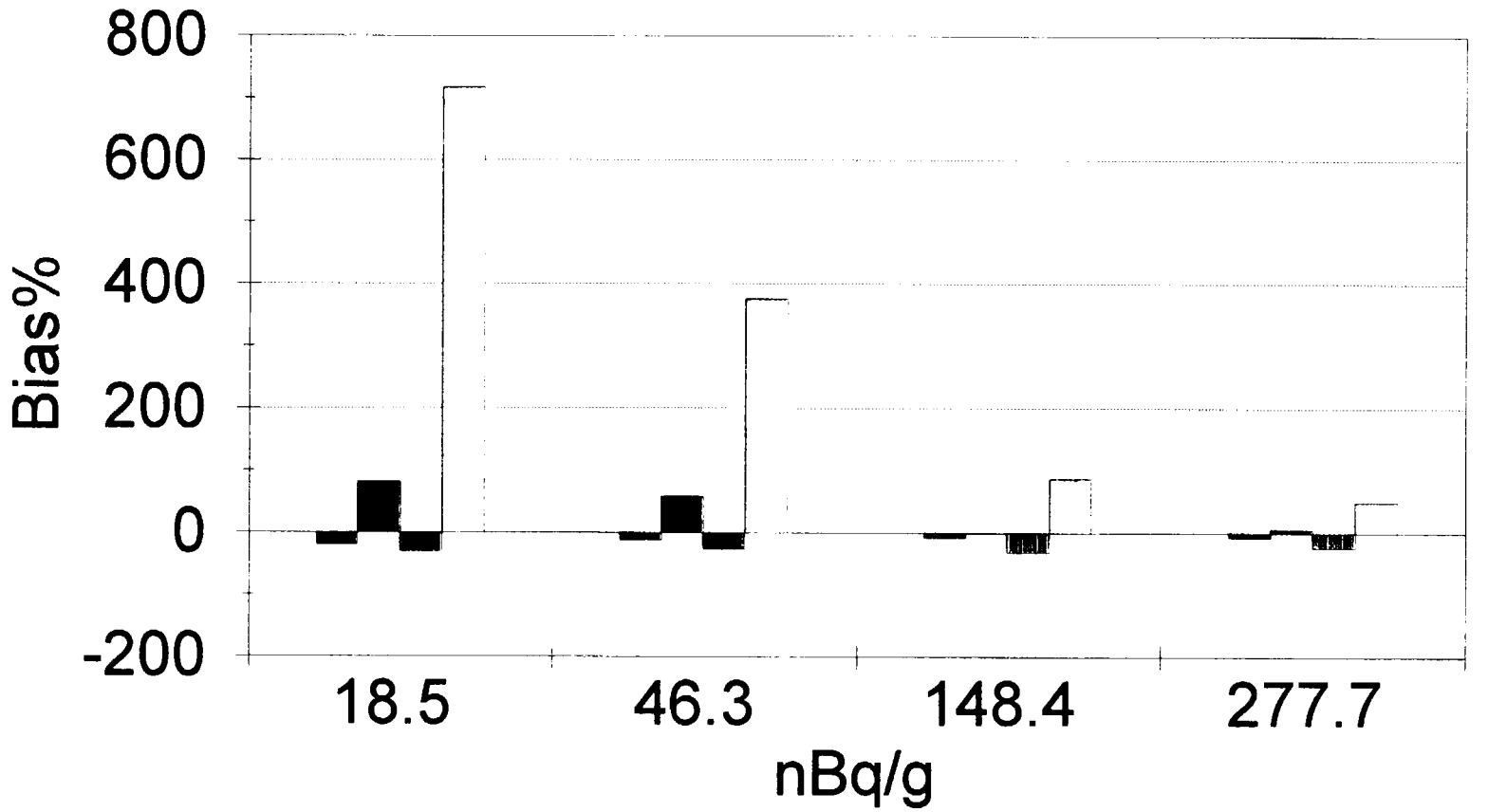
PNNL ICPMS Pu/Urine



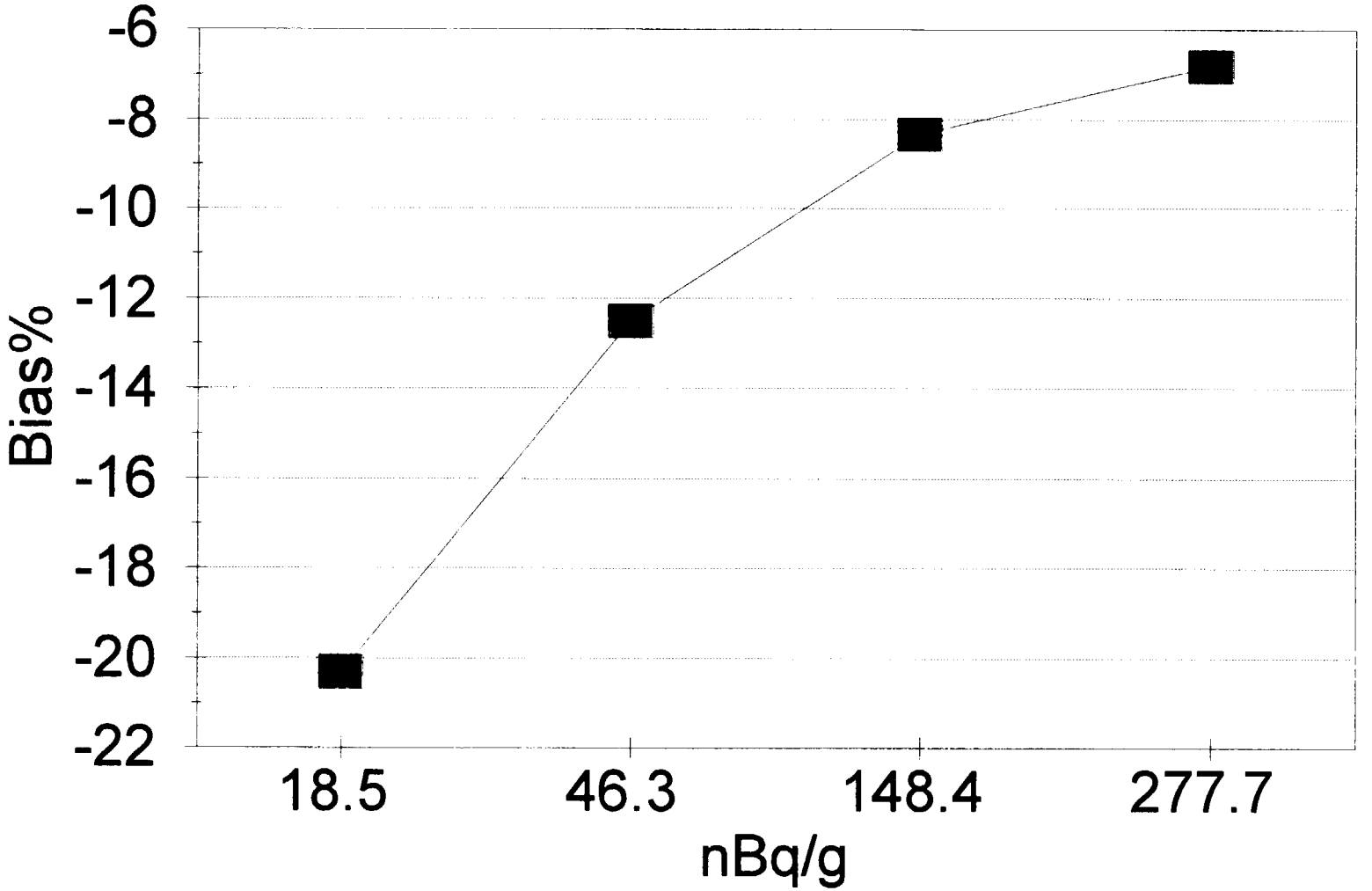
Figures 23-27

Bias

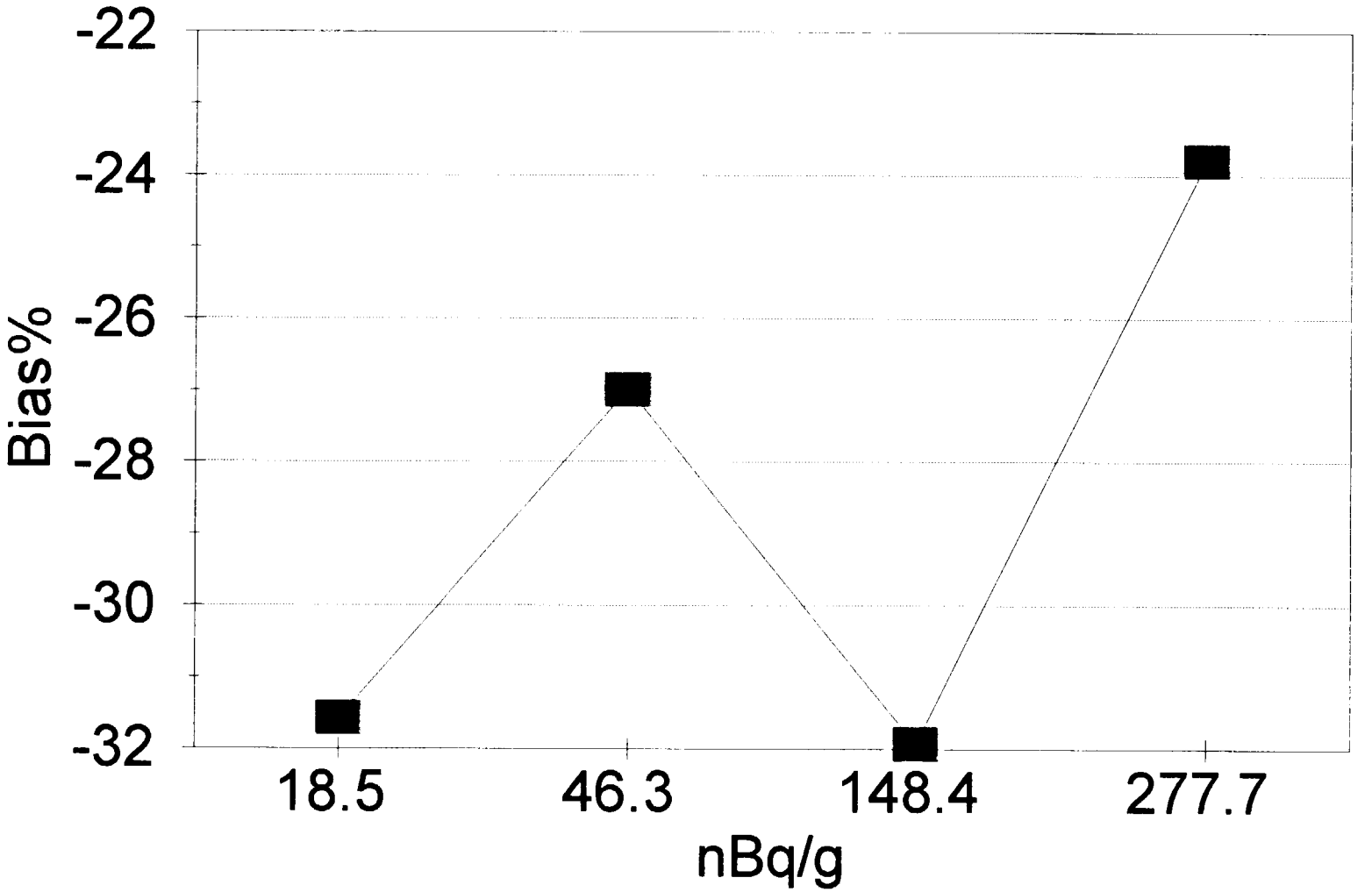
Pu in Urine


800
600
400
200
0
-200
Bias%
18.5
46.3
148.4
277.7
nBq/g
BNL-ICPMS
LANL
BNL-FTA
PNNL

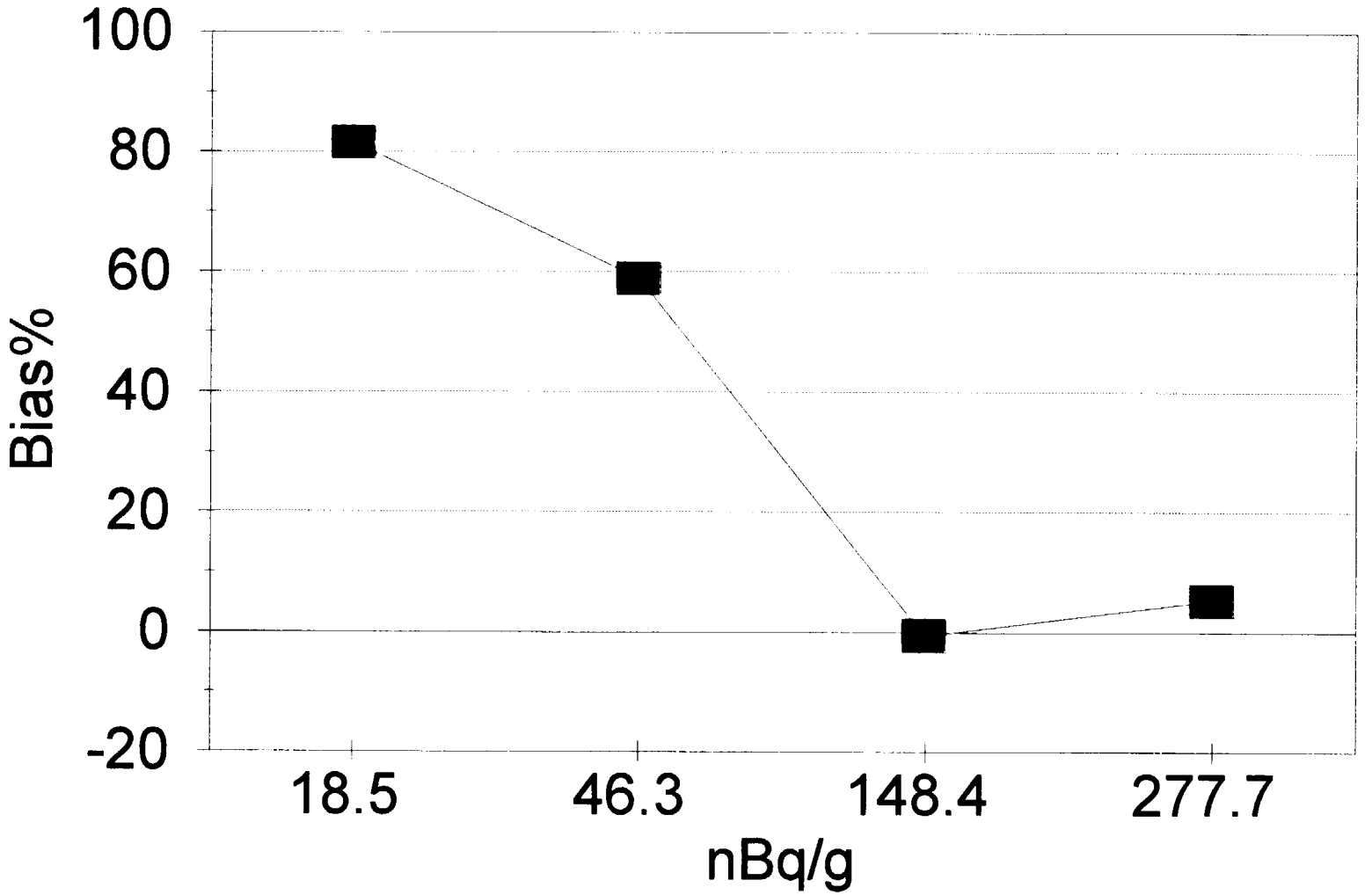
BNL ICPMS Pu/Urine



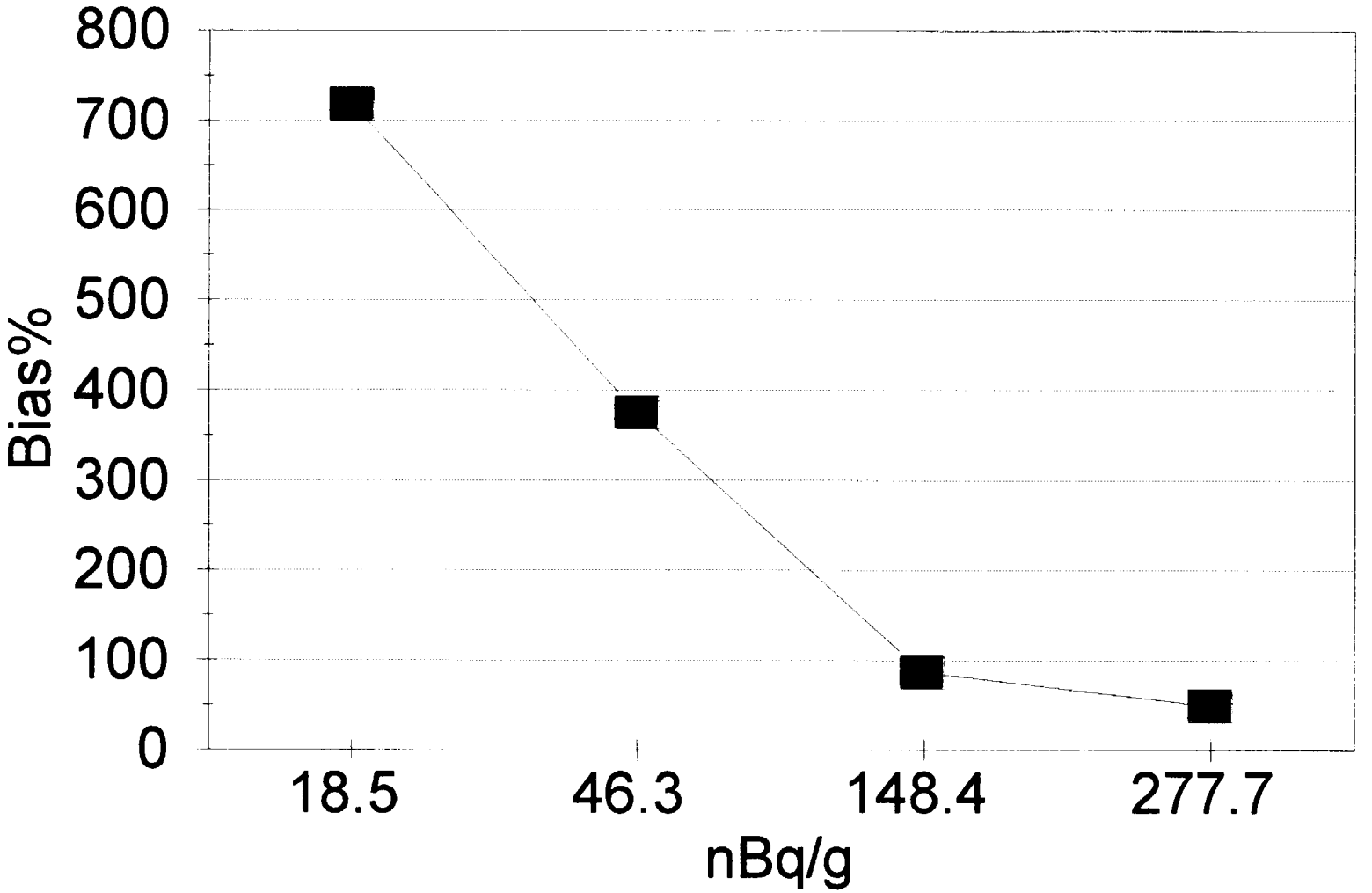
BNL FTA Pu/Urine



LANL TIMS Pu/Urine



PNNL ICPMS Pu/Urine



Spreadsheet 5

Minimum Detectable Amount

I	A	B	C	D	E	F	G	H	I
1	mda								
2									
3	lab	NIST	Reported	Random	Systemmatic	Random	Systemmatic	mda	mda
4		nBq/g	nBq/g	sm1%	sigma1%	sm1(nBq/g)	sigma1(nBq/g	nBq/g	at "0" nBq/g
5									
6	BNL ICP-MS	BLANK	-0.025	5931.55	10.7	1.4828875	0.002675	9.242649	7.9
7		18.5	14.8	6.416846	10.7	0.9496932	1.5836	6.993474	CL95% = 22%
8		46.3	40.5	2.589651	10.7	1.0488087	4.3335	7.40138	
9		148.4	136	0.600365	10.7	0.8164964	14.552	6.452636	
10		277.7	259	0.603574	10.7	1.5632567	27.713	9.593352	
11									
12	BNL FTA	BLANK	5.5	59.38157	18.9	3.2659864	1.0395	21.13697	6
13		18.5	12.7	6.029705	18.9	0.7657725	2.4003	6.826113	CL95% = 1900%
14		46.3	33.8	19.87761	18.9	6.7186322	6.3882	50.13683	
15		148.4	101	29.45857	18.9	29.753156	19.089	517.8243	
16		277.7	212	21.57653	18.9	45.742244	40.068	1122.893	
17									
18	LANL TIMS	BLANK	45.7	79.88091	0.287	36.505576	0.131159	131.1281	3
19		18.5	33.6	5.531462	0.287	1.8585712	0.096432	9.160743	CL95% = 585%
20		46.3	73.5	7.546218	0.287	5.5464702	0.210945	21.48596	
21		148.4	147	15.57221	0.287	22.891149	0.42189	81.55305	
22		277.7	292	28.3139	0.287	82.676588	0.83804	315.1431	
23									
24	PNNL ICP-M	BLANK	135	25.92593	22.4	35.000006	30.24	816.347	455
25		18.5	151	20.42172	22.4	30.836797	33.824	649.2829	CL95% = 3600%
26		46.3	220	45.45455	22.4	100.00001	49.28	5889.889	
27		148.4	276	29.55953	22.4	81.584303	61.824	3982.039	
28		277.7	414	9.373724	22.4	38.807217	92.736	985.7653	

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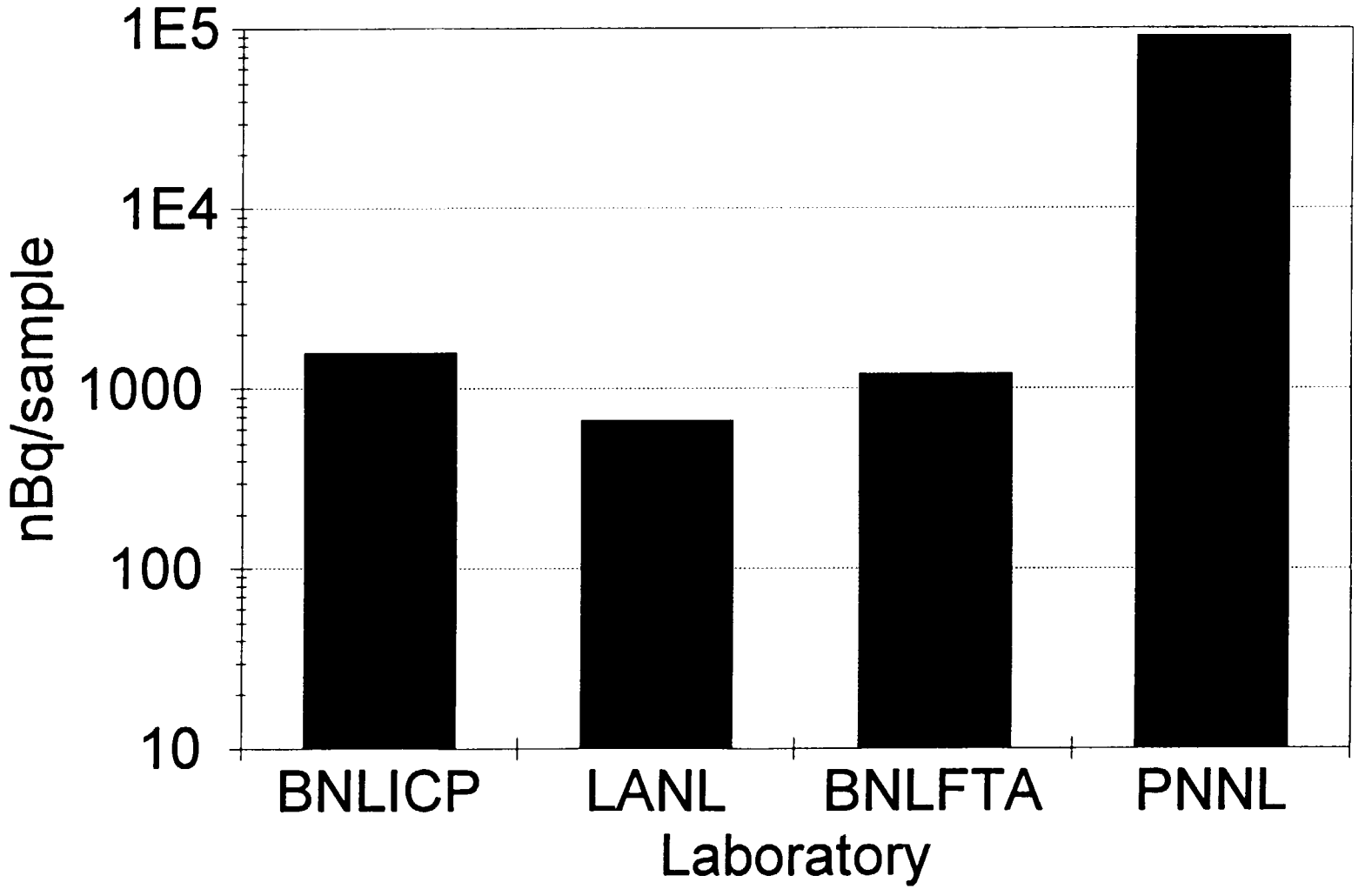
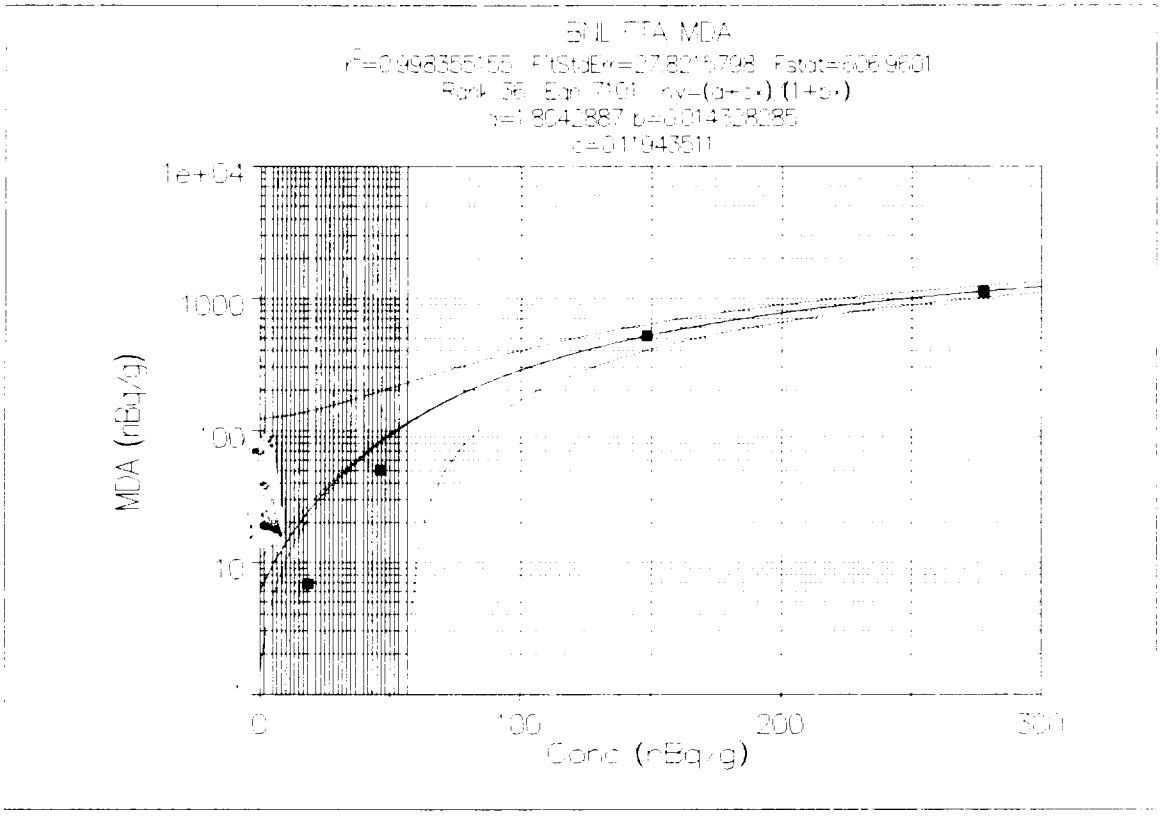
Figures 28-31

Minimum Detectable Amount

MDA Pu/Urine


1E5
1E4
1000
100
10
nBq/sample
BNLICP
LANL
BNLFTA
PNNL
Laboratory



BNL FTA MDA Sep 9,1997 11:26 PM

5 Active X-Y Points

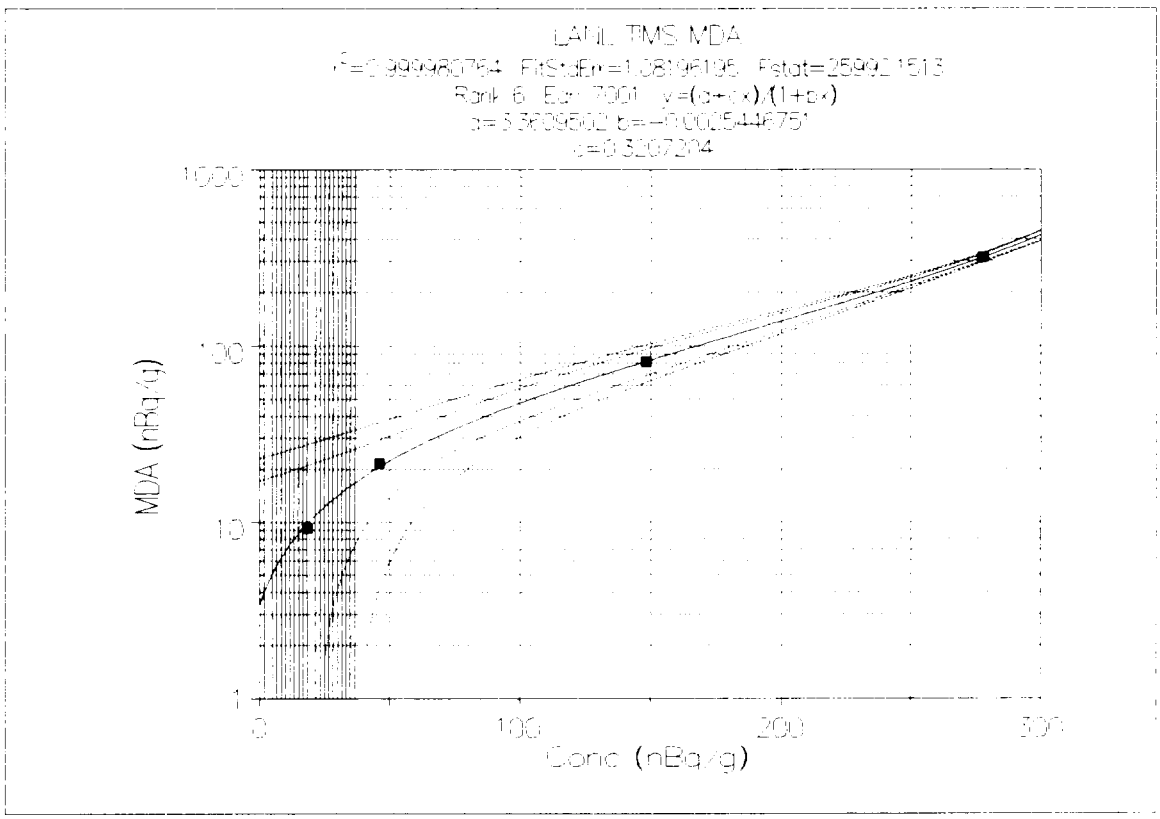
X: Conc (nBq/g)	Mean: 98.18	SD: 115.57381624
Y: MDA (nBq/g)	Mean: 343.7634426	SD: 485.06990265

File Source:

Rank 36 Eqn 7101 lny=(a+cx)/(1+bx)

r2 Coef Det	DF Adj r2	Fit Std Err	F-value
0.9983551552	0.9934206209	27.821579826	606.96010035

Parm	Value	Std Error	t-value	95% Confidence Limits	
a	1.804288718	1.121621043	1.608643783	-2.84635413	6.454931566
b	0.014328285	0.00460172	3.113680267	-0.0047521	0.033408666
c	0.119435114	0.036337588	3.286820091	-0.03123355	0.270103778



LANL TIMS MDA Sep 9,1997 11:33 PM

4 Active X-Y Points

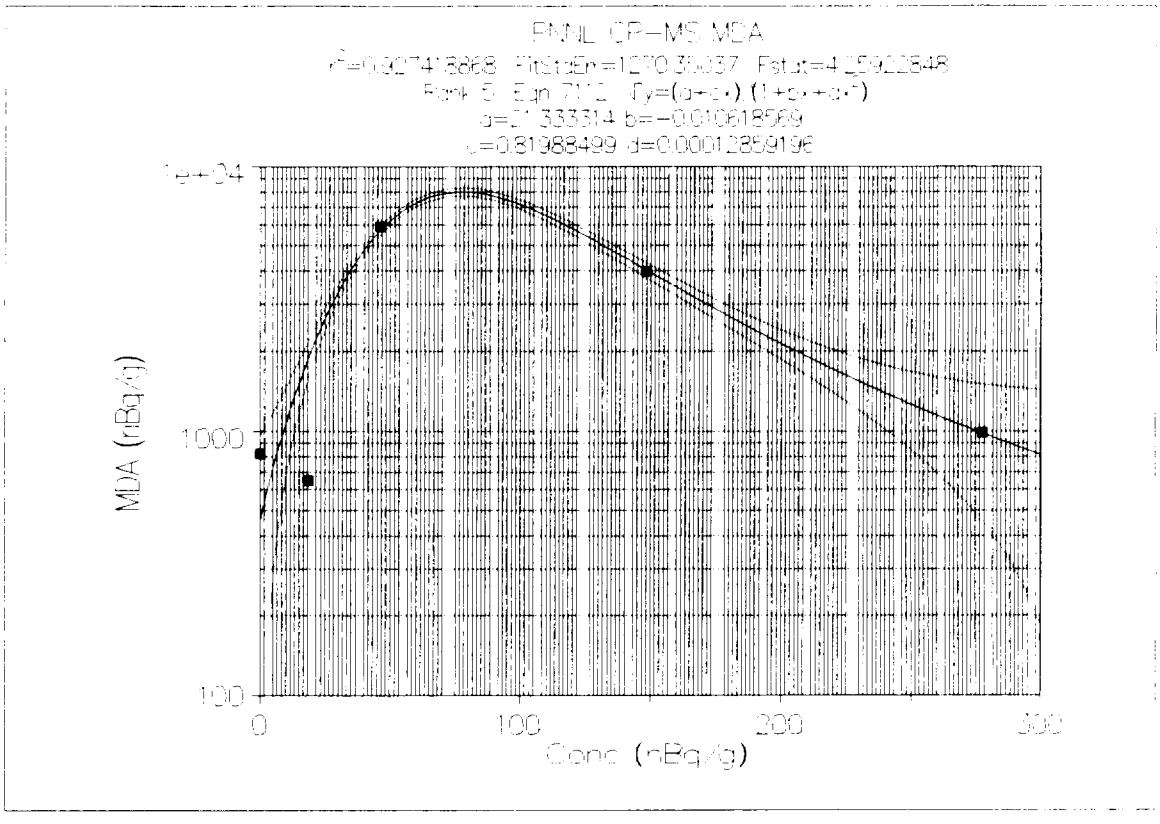
X: Conc (nBq/g)	Mean: 122.725	SD: 117.44514677
Y: MDA (nBq/g)	Mean: 106.83571325	SD: 142.42677724

File Source:

Rank 6 Eqn 7001 y=(a+cx)/(1+bx)

r2 Coef Det	DF Adj r2	Fit Std Err	F-value
0.9999807638	0.9999422914	1.0819619474	25992.151267

Parm	Value	Std Error	t-value	95% Confidence Limits	
a	3.360950177	1.068903689	3.144296544	-10.4214387	17.14333908
b	-0.00254468	4.15384e-05	-61.260773	-0.00308027	-0.00200908
c	0.320720403	0.014819793	21.64135539	0.129634761	0.511806046



PNNL ICP-MS MDA Sep 9,1997 11:47 PM
5 Active X-Y Points
X: Conc (nBq/g) Mean: 98.18 SD: 115.57381624
Y: MDA (nBq/g) Mean: 2464.66464 SD: 2357.6626151
File Source:

Rank 5 Eqn 7112 SQRTy=(a+cx)/(1+bx+dx2)

r2 Coef Det	DF Adj r2	Fit Std Err	F-value
0.9274188685	0.7096754739	1270.3503745	4.2592284846

Parm	Value	Std Error	t-value	95% Confidence Limits	
a	21.3333141	39.26795737	0.543275371	-484.985698	527.6523259
b	-0.01061857	0.007909886	-1.34244268	-0.11260824	0.091371098
c	0.819884989	1.062183822	0.771886157	-12.8758583	14.51562827
d	0.000128592	0.000114773	1.120405329	-0.00135128	0.001608465

VIII.

CONCLUSIONS

The prime objective of this study was to assess the current capabilities of FTA, ICP-MS and TIMS to measure μBq quantities of ^{239}Pu in urine. It is clear that all three methods have the capabilities to make such measurements. BNL's excellent ICP-MS work demonstrated that accurate and precise measurements are already a reality. This reality, however, is probably dependent on the laboratory's ability to minimize and control the analytical blank. Such control can only be achieved with highly skilled professionals, in dedicated ultra-clean laboratory facilities, with ultra-pure reagents. These requirements will be costly, but necessary. Measurements of such small quantities of plutonium is technically difficult, and lost data (21% in this study) or repeat analysis must be minimized with robust analytical and measurement procedures. Although FTA does not have the analytical precision of high quality ICP-MS, this study has demonstrated that it potentially has comparable MDA to ICP-MS. Unless the inherent disadvantages of FTA (batch yield correction, track overlap, and poor statistics) can be overcome, it is advantageous that a larger share of development resources be focused on mass spectrometric analyses. While TIMS did not provide the high accuracy and precision of BNL ICP-MS, it is likely that it too could be improved to be competitive and deserves development. Both ICP-MS and TIMS could enhance their capabilities considerably through minimization and control over analytical blank, higher chemical recovery, improved precision, and higher accuracy yield monitors. With future improvements in technology and techniques, it is anticipated that ICP-MS and TIMS will satisfactorily meet the ANSI N42.22 criteria for traceability and the ANSI N13.30 criteria for bias and precision, even at these amazingly low concentrations of plutonium in the complex urine matrix.

Secondarily, the technical issues of test sample preparation and stability have been addressed. This study has demonstrated that careful serial dilutions of the plutonium SRM over nine orders of magnitude to nBq/g concentrations can be done accurately, that the dilutions can be confirmed by measurement within a few percent, and the plutonium in synthetic urine remains stable and accessible for analysis (to within 5 percent) for at least a few weeks. The success of this study confirms the efficacy of the protocol to prepare these test materials.

IX.

RECOMMENDATIONS

It is recommended that improvements to the accuracy, precision and sensitivity of plutonium-in-urine Mass Spectrometry metrology for reliable DOE/EH occupational worker's health and safety, validating excretion models; identification of the source-terms; and litigation dispute resolution be initiated by:

1. Evaluating and contrasting techniques, during on-site assessments, of BNL, LANL and PNNL to determine the critical elements for success by the BNL ICP-MS:

    - o Evaluate sources of laboratory blank contamination,
    - o Evaluate why the Labs had difficulty with the Blanks,
    - o Evaluate why the Labs had low chemical yields,
    - o Evaluate why the Labs had large measurement imprecision,
    - o Evaluate why the Labs had analytical bias.

2. Developing a consistent method to calculate FTA and ICP-MS measurement uncertainties and detection limits.

3. Preparing Standard Reference Material ^{242}Pu at chemical yield tracer at 11.1 μBq/g level for use by the mass spectroscopy community.

4. Conducting intercomparison of ^{239}Pu in the range of 1500-100 aCi/200 mL of synthetic urine containing chemical and isobaric interferences: ^{240}Pu, ^{241}Pu, and trace-elements too more carefully test ICP-MS, TIMS and FTA under more realistic conditions.

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ACKNOWLEDGMENTS

The author gratefully acknowledges the expertise provided by David McCurdy and Leenu Kuruvella (YAEL), and the measurement expertise of Edward Kaplan (BNL), Peggy Gautier and Moses Attrep (LANL), and Eric Weiss (PNNL). The author also acknowledges the constant support by Neil M. Barss and R. Thomas Bell III (DOE-EH63) through contract number DE-AI01-96EH96203.